

Cuk-400467-7-P22765

**JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY**



VOLUME XVIII

1941

Title Page, Contents, Errata and Indexes



CALCUTTA UNIVERSITY PRESS

PRINTED IN INDIA
PRINTED AND PUBLISHED BY BHUPENDRALAL BANERJEE
AT THE CALCUTTA UNIVERSITY PRESS, 48, RA7RA ROAD, CALCUTTA

Reg. No. 1427P—July, 1942—G

(JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY)

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(VOLUME XVIII

1941)

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Vol. XVIII, 1941.

CONTENTS

	PAGE
1. Chemotherapy of Bacterial Infections. Part II. Chemistry of some Organo-selenium Compounds related to Sulphanilamide.— By P. L. Narasimha Rao 	1
2. Studies in Vitamin-C Oxidation. Part I. Co-existence of Oxi- dising and Protective Factors in Plants for Vitamin-C.—By P. V. Krishnamurthy and K. V. Giri 	7
3. Properties of Activated Sugar Charcoal coated with Various Organic Substances. Part III. Catalytic Decomposition of Hydrogen Peroxide.—By Harendra Kumar Acharya 	15
4. Oxalenediamidoxime. Part II.—By R. Chatterjee 	19
5. Acridine Derivatives. Part VI.—By S. J. Das-Gupta 	25
6. The Azo Compounds from Morphine. Part I.—By Amaresh Chandra Roy 	29
7. The Alkaloids of <i>Rauwolfia Canescens</i> , Linn. Part I.—By Miss Asima Mookerjee 	33
8. The Influence of Light on Nitrogen Fixation in Dacca Soil.—By M. Sulaiman 	40
9. A New Reagent for the Estimation of Mercury and Copper.—By S. J. Das-Gupta 	43
10. A Note on the Electrolytic Estimation of Lead as Peroxide.—By Dushyant Narasingasa Solanki and T. V. Subba Rao 	45
11. Resin Plastics.—By H. K. Sen 	47
12. Composition of Prussian and Turnbull's Blues. Part IV. Study of their Adsorptive Properties.—By Abani K. Bhattacharya 	71
13. Studies in the Camphor Series. Part VI.—By Dines Chandra Sen 	76
14. Composition of Prussian and Turnbull's Blues. Part V. Role of Hydrolysis and their Compositions.—By Abani K. Bhatta- charya 	81
15. Composition of Prussian and Turnbull's Blues. Part VI. Magnetic Susceptibility of the Compounds.—By Abani K. Bhatta- charya 	85
16. Studies on Optical Activity and Chemical Constitution. Part V.	

	Rotatory Powers of Camphoranilic Acids, α - and β -Naphthyl- camphoramic Acid at various Degrees of Neutralisation. —By Mahan Singh and Arjan Singh	89
17.	Acridine Derivatives. Part VII. Compounds with Mercury, Copper and Antimony.—By S. J. Das-Gupta	93
18.	Complex Chromi-selenates.—By Prodosh Chandra Raychoudhury	97
19.	The Conductometric Method of Determining the Soluble Salt Content of Soils for use in Soil Survey Work.—By R. C. Hoon, J. K. Malhotra and Lakshmi Chand Jain	103
20.	The Condensation of α -Substituted Acetoacetates with Phenols. Part III. The Pechmann Condensation of Ethyl α -(α -Hy- droxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate.—By D. R. Kulkarni, R. L. Alimchandani and N. M. Shah	113
21.	Quinoline Derivatives. Part VI.—By Debabrata Das-Gupta and Tejendra Nath Ghosh	120
22.	The Condensation of α -Substituted Acetoacetates with Phenols. Part IV. The Condensation of Cresols and other less Re- active Phenols with Ethyl α -(α -Hydroxy- $\beta\beta\beta$ -trichloroethyl)- acetoacetate.—By D. R. Kulkarni, R. L. Alimchandani and N. M. Shah	123
23.	Photosensitisation by Solids. Part II. Photosensitised Oxida- tion of Ammonia in Aqueous Solution with Titania as the Photosensitiser.—By G. Gopalarao and K. S. Murty	127
24.	Coagulation of Colloids by Exposure to High Frequency Oscil- lations.—By Shridhar Sarvottam Joshi and A. Purushottam	138
25.	The Influence of Vitamin-C on the Inactivation of Enzymes by Ultraviolet Light.—By K. V. Giri	141
26.	Co-ordinated Mercury Compounds with Ethylene- and Propylene- diamines.—By Panchanan Neogi and Kanai Lal Mondal	146
27.	Biguanide Sulphate as a Reagent for the Estimation of Copper. —By Priyadarajan Ray and Jaminibhusan Roy-Chowdhury	149
28.	The Use of Nitroso Derivatives as Reagents in Inorganic Ana- lysis. Part I.—By S. S. Guha-Sircar and Sasanka Chandra Bhattacharjee	155
29.	The Use of Nitroso Derivatives as Reagents in Inorganic Ana- lysis. Part II.—By S. S. Guha-Sircar and Sasanka Chandra Bhattacharjee	161
30.	A New Method of Preparation of Aceto- and Benzonitriles.—By Yeo Sem Gwan	164
31.	A New Colorimetric Method for the Chlorate ion.—By M. B. Roy	165

32.	A Note on Certain Heterocyclic Sulphonamides.—By U. P. Basu and S. J. Das-Gupta	167
33.	Iodination. Part I. Studies on the Equilibrium in Systems of Iodine and various Unsaturated Organic Compounds in the Dark in different Non-polar Solvents.—By J. C. Ghosh, S. K. Bhattacharyya, M. M. Dutt and M. J. Rao	171
34.	Electrodeposition of Cadmium on Iron.—By Dushyant Narasingasa Solanki and Bhaskar Govind Joshi	177
35.	Studies in Vitamin-C Oxidation. Part II. Influence of various Substances occurring in Plant and Animal Tissues on the Catalytic Oxidation of Vitamin-C.—By P. V. Krishnamurthy and K. V. Giri	191
36.	A New Synthesis of Eudalene.—By Nripendra Nath Chatterjee and Amalendu Bose	196
37.	Studies in Vitamin-C Oxidation. Part III. The Retardation of Vitamin-C Oxidation by Oxalic Acid.—By P. V. Krishnamurthy	201
38.	Sulphonamides. Part II.—By K. N. Gaiind, R. P. Sehgal and J. N. Ray	209
39.	New Method of Synthesis of <i>iso</i> Quinoline Derivatives.—By K. N. Gaiind, (Miss) S. Kapoor and J. N. Ray	213
40.	Complex Compounds of Biguanide with Bivalent Metals. Part III. Nickel Biguanidines.—By Priyadarajan Rây and Bhupesh Chandra Purakayastha	217
41.	The Phenylthiocarbamides. A Contribution to the Study of the Triad -N'C'S-. Part X. Action of Hydrolytic Agents, Alkaline Lead Acetate and Nitrous Acid on Thiosemicarbazide.—By Ramchandra Sahasrabudhey and Hans Krall	225
42.	Decomposition of Potassium Nitrate in Sunlight.—By T. V. Subba Rao and G. Gopal Rao	229
43.	A New Synthesis of Cadalene.—By Phanindra Chandra Dutta	233
44.	Apparent Molal Volumes of Electrolyte Mixtures in Aqueous Solution.—By Amritansu Sekhar Chakravarti and Balbhadra Prasad	239
45.	Iodination. Part II. Studies on the Iodination of Different Unsaturated Organic Compounds in the Dark in Different Non-polar Solvents.—By J. C. Ghosh, S. K. Bhattacharyya, M. M. Dutt and M. J. Rao	245
46.	Iodination. Part III. Studies on the Iodination of Different Un-	

	PAGE
saturated Organic Compounds in the Dark in Polar Solvents. —By S. K. Bhattacharyya and M. J. Rao	253
47. Iodination. Part IV. Studies on the Photo-iodination of Different Unsaturated Organic Compounds in Light of Different Frequencies in Non-polar Solvents.—By S. K. Bhattacharyya ..	257
48. Iodination. Part V. Studies on the Photo-iodination of Phenylacetylene in Light of Different Frequencies in Polar Solvent. —By S. K. Bhattacharyya	269
49. The Detection and Determination of Pyridine Bases in Dehydrated Spirit.—By H. D. Suri, Gurcharan Singh Ahluwalia and H. B. Dunncliff	273
50. On the Study of the Dehydration of some Pure and Mixed Chromi-selenic Alums and the Formation of Corresponding Complex Chromi-selenates.—By Prodosh Chandra Raychoudhury	277
51. The Sensitisation Spectra of certain Cyanine Dyes derived from α -Picoline.—By M. Q. Doja	281
52. Variations in the Electrochemical Properties of Silicic Acid and Hydrogen Bentonite Soils with Temperature.—By Jnanendra Nath Mukherjee, Baradananda Chatterjee and Amitabha Sen	283
53. Complex Compounds of Biguanide with Tervalent Metals. Part VIII. Resolution of Cobaltic <i>tris</i> Biguanide. Complex into its Optically Active Enantiomerides.—By Priyadarajan Rây and Nihar Kumar Dutt	289
54. Complex Compounds of Biguanide with Tervalent Metals. Part IX. Action of Mercuric Chloride and Silver Nitrate upon Chromium and Cobaltic <i>tris</i> Biguanidinium Hydroxides and the Constitution of Biguanide Metal Complexes.—By Priyadarajan Rây and Sushil Kumar Siddhanta	298
55. The Ternary System. Ammonium Nitrate—Ammonium Sulphate—Water at 25°.—By R. K. Bahl and Surjit Singh	307
56. The Action of Hydrogen Sulphide on Permanganates. Part I. Calcium and Silver Permanganates.—By Sardar Mohammad and Ganga Singh Ahluwalia	309
57. Chemotherapy of Bacterial Infections. Part III. <i>N</i> '- β -Phenylethylsulphanilamides.—By P. L. Narasimha Rao	316
58. Adsorption of Polybasic Organic and Inorganic Acids. Discontinuities in Adsorption Process from Solutions of Sugar Charcoal.—By Kesho Dass Jain and J. B. Jha	321

CONTENTS

v

PAGE

59.	Determination of Copper in Country Spirits.—By H. D. Suri, Gurcharan Singh Ahluwalia and H. B. Dunnicliff	326
60.	The Fatty Oil from the Seeds of <i>Solanum Indicum</i> , Linn.—By S. V. Puntambekar and S. Krishna	329
61.	Periodates of Quadrivalent Metals.—By Prodosh Chandra Raychoudhury	335
62.	Studies in Hydrogen Bond Formation. Part I. Amides.—By A. L. Sundara Rao	337
63.	Magnetism and Catalysis Part III. Chlorination of Chloroform to Carbon Tetrachloride in presence of Ferric Chloride.—By S. S. Bhatnagar, N. A. Yajnik, P. L. Kapur and Anand Swaroop Bhatnagar	350
64.	The Action of Chlorine on the Hydroxides of Iron and Chromium in the presence of Iodine.—By R. K. Bahl and Manohar Lal	359
65.	Photosensitisation of Solids. Part III. Photosensitised Oxidation of Ammonia in Aqueous Solution with Colloidal Titania as the Photosensitiser.—By G. Gopal Rao and Ch. I. Varadanam	361
66.	Magnetism and Catalysis. Part IV. Catalysis of the Reaction between Ammonium Oxalate and Mercuric Chloride by Ferric Ions —By S. S. Bhatnagar, P. L. Kapur, Anand Swaroop Bhatnagar and Brahm Prakash	371
67.	Micro-analytical Method for the Estimation of Ferrous and Ferric Iron in Minerals.—By Jyotirmoy Das-Gupta	375
68.	Microchemical Investigations on Spotted Muscovite Mica.—By Jyotirmoy Das-Gupta	381
69.	Complex Formation by Ascorbic Acid with Formaldehyde.—By P. V. Krishnamurthy	383
70.	Magnetism and Catalysis. Part V. A Magnetic Study of the Catalytic Decomposition of Potassium Chlorate by Cobaltous Oxide and Ferro-magnetic Variety of Ferric Oxide.—By S. S. Bhatnagar, P. L. Kapur, Anand Swaroop Bhatnagar and M. A. Qayyum	391
71.	On the Composition and Constitution of Paramolybdates —By Priyadarshan Ray and Sushil Kumar Siddhanta	397
72.	Studies in Enzymes. Amylase from Kaseru (<i>Scirpus Grossus</i> , Linn) —By J. P. Shukla	407
73.	On a Relationship between Refractive Index and Surface Tension.—By R. C. Tripathi	411
74.	Oxanilic Acid Thioamide as an Analytical Reagent.—By Anil Kumar Majumdar	415

	PAGE
75. Quinoline-8-carboxylic Acid as an Analytical Reagent. Part I. —By Anil Kumar Majumdar	419 .
76. Studies of some Physical Factors in the Electrodeposition of Nickel on Iron.—By Dushyant Narasingasa Solanki and Damri Singh	423
77. Adsorptive Properties of Synthetic Resins. Part V.—By S. S. Bhatnagar and M. Sarup	447
78. Some New Reactions of <i>r</i> -Benzylidenecoumaran-2-ones. Part I. —By T. B. Panse, R. C. Shah and T. S. Wheeler	453
79. Raman Spectra of Substituted Sulphuric Acids. Part I.—By Jagannath Gupta and Anil Kumar Majumdar	457
80. Studies in Long-chain Acids Part III. On <i>bis</i> -nor-Oleic Acid. —By P. C. Mitter and Phanindra Nath Bagchi	461
81. The Effect of Colloids on the Electrodeposition of Nickel on Copper.—By V. S. Puri and S. R. Seth	465
82. 9-Thiophenanthrene and some of its Derivatives.—By Paresh Chandra Dutta	469
83. On the Velocity of Hydration and Dehydration of Nickel Sulphate. —By B. N. Ghosh	472
84. Azine Dyes Derived from 9,10-Phenanthrathiophene-2':3'-dione. —By Paresh Chandra Dutta and Ramani Mohan Sinha	477
85. Structure of Oxymethylene Methyl Ethyl Ketone and of Oxyme- thylene Methyl- β -phenyl Ethyl Ketone.—By S. N. Joshi, R. Kaushal and S. S. Deshapande	479
86. The Alkaloids of <i>Rauwolfia Canescens</i> , Linn. Part II.—By Miss Asima Mookerjee	485
87. On the Moving Boundary Method for the Determination of Cataphoretic Speed of Colloids. Part II.—By N. C. Sen- Gupta and P. R. Sinha	489
88. Reaction between Glucose and Iodine in Alkaline Medium. Effect of Neutral Salts.—By Kesho Dass Jain and B. L. Vaish	503
89. A Note on an Isomer of Dimethylethylpyridine.—By Rafat Husain Siddiqui	505
91. Studies on the Photochemical Activity of Mixtures of Vanadic Acid and Tartaric Acid. Part I. Optical Properties of Mixtures of Vanadic Acid and Tartaric Acid. Reduction of these Mixtures in Light and in the Dark.—By T. L. Rama Char	507
92. Spectrum Analysis of Mineral Contents of Fruits.—By L. Sibaiya and M. S. Venkatasubba Rao	523

93.	Base-exchange of Mercuric Ions Adsorbed on Wool.—By C. S. Narwani and G. T. Gursahani	527
94.	Rhythmic Precipitation of Silver Chloride in Gelatin Tanned with Chromium Chloride.—By C. S. Narwani and G. T. Gursahani	531
95.	Adsorption of Hydroxybenzenes by Sugar Charcoal. Discontinuities in the Adsorption of Phenol, Resorcinol and Quinol from Aqueous Solutions.—By Kesho Dass Jain and J. B. Jha	535
96.	The Magnetic Susceptibilities of Metallic Oxides and their Molecular Structures with Special Reference to those of Cobalt.—By S. S. Bhatnagar, Brahm Prakash and Mohammed Abdul Qayyum	540
97.	The Seed Fat of <i>Buchanania Latifolia</i> .—By N. N. Godbole, B. G. Gunde and P. D. Srivastava	557
98.	Studies on the Photochemical Activity of Mixtures of Vanadic Acid and Tartaric Acid. Part II. Photocatalysis by Colloidal Micelle obtained by the Reduction of Vanadic Acid and Tartaric Acid. Induced Optical Activity by Circularly Polarised Light.—By T. L. Rama Char	563
99.	Normal Aluminium Chromate.—By Prodosh Chandra Raychoudhury	573
100.	Periodates of Trivalent Metals.—By Prodosh Chandra Raychoudhury	576
101.	The Colorimetric (<i>p</i> -Dimethylaminobenzaldehyde—Sulphuric Acid) Method for Determining small Quantities of Atropine.—By R. P. Daroga	579
102.	Estimation of Copper in presence of Iron.—By P. L. Kapur and Badar-ud-Din	585
103.	Estimation of Iodine in Periodates.—By R. K. Bahl, Surjit Singh and Narindra K. Bali	587
104.	A Note on the New Formula for Chaksmc.—By S. Siddiqui and Z. Ahmad	589
105.	A Note on the Separation of Silicon and Tin in Tin-silica Mixture, Welding Brasses and Silicon Brasses by Alkali Sulphate.—By D. P. Chatterjee	591
106.	Studies on the Photochemical Activity of Mixtures of Vanadic Acid and Tartaric Acid. Part III. Induced Circular Dichroism in Vanadic Acid Sol. Photoreduction of Dichroic Sol by Tartaric Acid in Circularly Polarised Light—By T. L. Rama Char	605

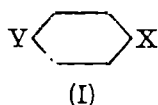
107.	Complex Compounds of Biguanide with Bivalent Metals. Part III Copper and Nickel Phenylbiguanidines and their Different Modifications.—By Priyadarajan Rây and Kshitishranjan Chakravarty	609
108.	Electrochemical Preparation of Sodium Chlorate from Aqueous Sodium Chloride.—By Shridhar Sarvottam Joshi and K. Srinivasan	623
109.	Kinetics of Hydrogenation of Oils in a Continuous Process.—By R. V. Joglekar and S. K. K. Jatkar	631
110.	Studies in the Substituted Succinic Acids. Part I.—By Rafat Husain Siddiqui and Salah-ud-din	635
111.	A Method of preparing Mono-ethers of Methyleneglycol.—By M. L. Gupta, R. Kaushal and S. S. Deshapandé	638
112.	Chemical Examination of <i>Thalictrum Foliolosum</i> D.C. Isolation and Characterisation of a new Alkaloid, Thalictrin.—By Shiam Kishore Vashistha and Salimuzaman Siddiqui	641
113.	Variations in the Electrochemical Properties of Hydrogen Clay Sols with Temperature.—By B. Chatterjee and A. Sen	646
	Reviews	169, 286, 555
	Obituary	387

CHEMOTHERAPY OF BACTERIAL INFECTIONS. PART II. CHEMISTRY OF SOME ORGANO-SELENIUM COMPOUNDS RELATED TO SULPHANILAMIDE.

By P. L. NARASIMHA RAO.

The chemistry of some 4:4'-substituted diphenylphenyl diselenides, selenides, 4-substituted seleninic, selenonic acids and selenophenols has been described.

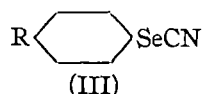
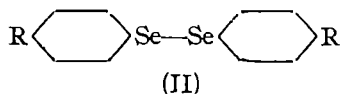
Antibacterial or antiprotozoal drugs mostly conform to the structure I ($X = \text{As, Sb, Bi, Hg or S; } Y = \text{OH, NH}_2$).



It appears that the nature of these characteristic residues (I, X) exerts a profound influence on the capacity of a drug for causing competitive inhibition of a vital enzymic function in bacterial metabolism in which *p*-amino-benzoic acid is rendered inoperative. It was felt desirable to ascertain how the therapeutic action is augmented by the replacement of these residues (I, X) by those of other related elements *e.g.*, selenium and tellurium which possess intrinsic antibacterial action.

Despite a large volume of work on sulphanilamide compounds, very few systematic attempts appear to have been made to study selenium and tellurium analogues similar to the arsenical, antimony and bismuth drugs, and in the present communication the results of a preliminary study of the chemistry of some selenium compounds are reported.

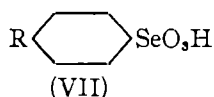
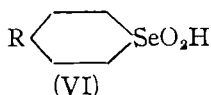
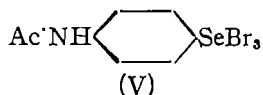
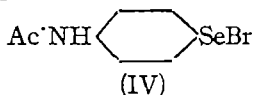
4:4'-Diacetyldiaminodiphenyl diselenide, m.p. 204-6° (II, $R =$



NHAc), is easily prepared from 4-acetylaminophenyl selenocyanate (III; $R = \text{NHAc}$) obtained by the interaction of 4-acetylaminophenyldiazonium acetate and potassium selenocyanate (Challenger and Peters, *J. Chem. Soc.*, 1928, 1375).

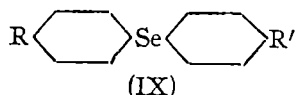
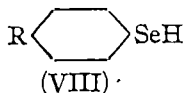
The free diamine (II, $R = \text{NH}_2$) may be readily obtained from the diacetyl derivative by hydrolysis (*cf.* Keimatsu, *J. Pharm. Soc. Japan*, 1933, 53, 203).

The diacetylaminodiphenyl diselenide as well as the selenocyanate (III, $R = \text{NHAc}$) readily furnish the monobromo (IV) and tribromo (V) compounds, which unlike the corresponding nitro compounds (III and II, $R = \text{NO}_2$), give very little of the seleninic acid (II, $R = \text{NHAc}$) with boiling water, but give instead, a substance (m.p. $168-70^\circ$) which is being investigated.



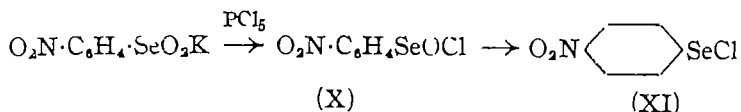
Among the acids of this series (*cf.* Pyman, *J. Chem. Soc.*, 1919, 115, 166; Challenger and Peters, *loc. cit.*), 4-acetylaminophenylseleninic acid (VI, $R = \text{NHAc}$) proved difficult to isolate in a state of purity but the corresponding benzoyl derivative (VI, $R = \text{NHPhCO}$) is easily isolated. The selenonic acids (VII, $R = \text{NO}_2$, NHAc , NHPhCO) are readily obtained as their potassium salts by the oxidation of the seleninic acids with aqueous permanganate (Pyman, *loc. cit.*).

Of the selenophenols (VIII) investigated, the 4-nitroselenophenol (VIII, $R = \text{NO}_2$) is found to be extremely unstable being converted



immediately into the diselenide (II, $R = \text{NO}_2$).

However, 4:4'-dinitrodiphenyl selenide (IX, $R = R' = \text{NO}_2$) has been prepared *via* (VIII, $R = \text{NO}_2$), which is an intermediate product. This method of preparation of selenides is being extended to include mixed ones (IX). The results of these experiments will be published later. For the preparation of selenium analogues of sulpanilamide, potassium 4-nitrophenylseleninate has been reacted with phosphorus pentachloride. The product formed is (XI) instead of (X).



In presence of aqueous ammonia or ice-water (XI) gives only a mixture of 4:4'-dinitrodiphenyl diselenide (II, $R = \text{NO}_2$) and 4-dinitrophenylseleninic acid (VI, $R = \text{NO}_2$) by disproportionation (*cf.* Behaghalt and Seibert, *Ber.*, 1933, 86B, 708).

E X P E R I M E N T A L.

4:4'-Dinitrodiphenyl Diselenide (II, $R=NO_2$).—A few preliminary experiments carried out to ascertain whether the substance could be obtained directly from 4-nitrophenyldiazonium acetate and sodium polyselenide by the method of Schoeller (*Ber.*, 1919, **82**, 1517) were not satisfactory as yields were invariably low. It was eventually prepared from 4-nitrophenyl selenocyanate (III, $R=NO_2$). Interaction of 4-nitrochloro- or bromobenzene and sodium selenide in alcoholic solution in presence of excess of selenium appears to give (IX; $R=R'=NO_2$) mixed with a little of (II, $R=NO_2$) (*cf.* Baker and Moffit, *J. Chem. Soc.* 1930, 1726).

4-Acetylaminophenyl selenocyanate (III, $R=NHAc$), described by Challenger and Peters (*loc. cit.*), was prepared more satisfactorily as follows. The diazonium chloride solution, prepared from *p*-acetylphenylenediamine (10 g.), was rendered neutral to congo red by the addition of sodium acetate and poured in a thin stream into a warm solution of potassium selenocyanate (9.8 g. in 30 c.c. of water at 60°) with stirring. After allowing the mixture to stay for 12 hours at room temperature, the precipitated light yellow solid was collected, washed thoroughly with cold water and crystallised twice from hot spirit (*norit*), m.p. 205.6°, yield 12.5 g.

4-Aminoselenophenol (VIII, $R=NH_2$).—A solution of the above selenocyanate (10 g.) and 2.5*N*-alcoholic sodium hydroxide (50 c.c.) was boiled under reflux for 6 hours. After partial evaporation of alcohol under reduced pressure, water (50 c.c.) was added and the solution exactly neutralised with acetic acid and aqueous ammonia. The precipitated selenophenol was quickly collected and crystallised from air-free dilute alcohol. After drying in a desiccator filled with nitrogen, it had m.p. 76–78°. (Found: N, 8.0. C_6H_7NSe requires N, 8.13 per cent). The aminoselenophenol is soluble in dilute sodium hydroxide and hydrochloric acid, but from concentrated solution, the hydrochloride crystallises out.

4-Acetylaminoselenophenol (VIII, $R=NHAc$).—In the above experiment if only 1/3 of the quantity of alcoholic potassium hydroxide was employed and the time of boiling reduced to only 1/2 hour, the hydrolysis stops at the stage of 4-acetylaminoselenophenol. It crystallises from dilute alcohol (nitrogen atmosphere) in pale yellow spangles, m.p. 160–65°. (Found: N, 6.4. C_6H_8ONSe requires N, 6.55 per cent). The sample of the substance, as obtained above, dissolves almost completely in air-free sodium hydroxide solution leaving but a few specks.

The selenophenol can also be obtained by a careful reduction of the selenocyanate with ammonium sulphide. If this reduction is carried in a

more drastic manner, some 4:4'-diacetyldiaminodiphenyl selenide (IX, $R=R'=NHAc$), m.p. 219° , is obtained (*cf.* D. R. P., 633,344) (Found: N, 8.3. $C_{18}H_{16}O_2N_2Se$ requires N, 8.07 per cent).

4:4'-Di-(acetylaminophenyl) Diselenide (II, $R=NHAc$).—The above selenophenol was oxidised with dilute hydrogen peroxide in a similar manner to that described by Keimatsu *et al.* (*loc. cit.*). It was crystallised first from dilute acetic acid and then from dilute alcohol (charcoal). From the latter solvent it crystallised in pale yellow spangles or long plates, m.p. $204-5^{\circ}$ with previous softening at $180-82^{\circ}$. (Found: N, 6.7. $C_{18}H_{16}O_2N_2Se_2$ requires N, 6.72 per cent). It is easily soluble in most organic solvents and very sparingly in boiling water.

4:4'-Diaminodiphenyl Diselenide (II, $R=NH_2$) was obtained directly from selenocyanate (III, $R=NHAc$; *cf.* Keimatsu *et al.*, *loc. cit.*) by first following the procedure described under 4-aminoselenophenol. The product without isolation was subjected to the action of atmospheric oxygen or hydrogen peroxide as described by Keimatsu. It is freely soluble in the usual organic solvents except petrol. From benzene, it crystallised in rosettes of pale orange-yellow crystals, but from lukewarm dilute alcohol it separated in pale yellow leaflets. The acid solutions of the amine easily decomposed and selenium was deposited. The sparingly soluble sulphate of the amine had m.p. $210-15^{\circ}$ (decomp.). (Found: N, 6.0. $C_{12}H_{12}N_2Se_2$, H_2SO_4 requires N, 6.33 per cent). The diacetyl derivative, prepared directly from the pure diamine, m.p. 80° , and acetic anhydride in pyridine solution in the ice-cold temperature for 3 days, required many crystallisations from alcohol. The dibenzoyl derivative, prepared in a similar way, separated from pyridine (charcoal) in pale yellow amorphous powder, m.p. $265-67^{\circ}$ (decomp.). (Found: N, 4.9. $C_{26}H_{20}O_2N_2Se_2$ requires N, 4.81 per cent). Dicaproyl (Found: N, 5.2. $C_{24}H_{32}O_2N_2Se_2$ requires N, 5.2 per cent) and divaleroyl derivative (Found: N, 5.3. $C_{22}H_{28}O_2N_2Se_2$ requires N, 5.49 per cent), obtained in a like manner, crystallised in leaflets from dilute alcohol, m.p. $175-77^{\circ}$ and $172-73^{\circ}$ respectively.

Potassium 4-Nitrophenylselenonate (VII, $R=NO_2$).—4-Nitrophenylseleninic acid was prepared according to the method of Behaghali and Siebert (*loc. cit.*). This acid (25 g.) was neutralised with ammonia and oxidised with hot aqueous solution of potassium permanganate solution (12.4 g.). After boiling for a short time, manganese dioxide was filtered and the filtrate carefully evaporated under reduced pressure till crystallisation started. The colourless prism-like crystals were collected after cooling, washed with a little ice-cold water and dried. It crystallised with water of crystallisation which was lost gradually even at the room temperature. (Found: N, 5.0. $C_6H_4O_5NKSe$ requires N, 4.86 per cent).

4-Benzoylaminophenylseleninic Acid (VI, $R = \text{NHPhCO}$).—Dry, powdered 4:4'-di-(benzoylaminophenyl) diselenide (II, $R = \text{NHPhCO}$) (10 g.) was gradually stirred into concentrated nitric acid (d 1.4, 40 c.c.) at -6° to -3° and the ice-cold mixture after keeping for 24 hours in an ice-chest was neutralised by dropping into ammonia maintained at 0.5° . The solution was filtered through charcoal and acidified with acetic acid. The precipitated powder was washed twice with ice-cold water and crystallised from boiling water. It separated in pale hay-coloured shining plates, m.p. 186° (decomp.). (Found: N, 4.8. $\text{C}_{13}\text{H}_{11}\text{O}_3\text{NSe}$ requires N, 4.54 per cent).

Potassium 4-benzoylphenylselenonate (VII, $R = \text{NHPhCO}$), prepared in a similar manner to the 4-nitro analogue, separated in dirty white crystals from water. (Found after drying at 110° : N, 4.0. $\text{C}_{13}\text{H}_{10}\text{O}_4\text{NKSe}$ requires N, 3.86 per cent).

Silver 4-Acetylaminophenylseleninate (VI, $R = \text{NHAc}$).—After following the same procedure described under 4-benzoyl analogue, the sparingly soluble silver salt was precipitated as a powder which decomposed on keeping. (Found: Ag, 29.9. $\text{C}_8\text{H}_8\text{O}_3\text{NAgSe}$ requires Ag, 30.27 per cent).

4-Aminophenylseleninic acid (VI, $R = \text{NH}_2$) was obtained as barium salt by hydrolysis of the benzoyl or acetyl derivatives with barium hydroxide. [Found after drying: Ba, 25.5. $(\text{C}_6\text{H}_5\text{O}_2\text{NSe})_2\text{Ba}$ requires Ba, 25.25 per cent].

4:4'-Dinitrodiphenyl Selenide (IX, $R = R' = \text{NO}_2$).—A mixture of 4-nitrophenyl selenocyanate (2.28 g.), *p*-bromonitrobenzene (2.05 g.) and potassium carbonate (1.1 g.) in aqueous alcoholic solution was refluxed for 2 days. The pale greenish yellow crystalline product was collected while still hot, washed once with a little hot alcohol and then with water, and finally crystallised twice from ethyl acetate (charcoal). The selenide separated in shining pale yellow prisms, m.p. 175° (Baker and Moffit, *loc. cit.*, recorded 170.71°). A mixture of the selenide and 4:4'-dinitrodiphenyl diselenide (II, $R = \text{NO}_2$) melted at 150.53° and it could not be separated into components easily by crystallisation.

4:4'-Diaminodiphenyl Selenide (IX, $R = R' = \text{NH}_2$).—After the hydrolysis of the diacetyl derivative by alcoholic potash, the product was crystallised from aqueous alcohol in yellowish shining plates, m.p. 115.17° . (Found: N, 10.4. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{Se}$ requires N, 10.64 per cent). It was also obtained from the corresponding nitro compound by reduction. The statement of Baker and Moffit (*loc. cit.*), about the reduction of *pp'*-dinitrodiphenyl selenide would appear to be erroneous. It is likely they mean only the reduction of diselenide (II, $R = \text{NO}_2$) and not the monoselenide (IX, $R = R' = \text{NO}_2$).

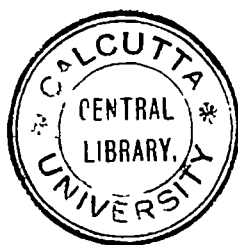
4-Acetylaminophenyl Selenotribromide (V).—To a well-cooled mixture of 4-acetylaminophenyl selenocyanate (III, R=NHAc, 7.8 g.) and chloroform (25 c.c.), bromine (3.3 c.c.) was added and after 24 hours, the separated orange-red rosettes of crystals (m.p. $130-32^{\circ}$, decomp. with previous softening at 100°) were collected and washed with chloroform-benzene mixture. (Found: Br, 54.2. $C_7H_4ONBr_3Se$ requires Br, 54.89 per cent).

4-Acetylaminophenyl Selenobromide (IV).—Finely powdered tribromide (V) lost two atoms of bromine when kept for a week in an evacuated desiccator over potassium hydroxide. The orange-red colour of the product turned to light yellow. (Found: Br, 29.1. $C_7H_4ONBrSe$ requires Br, 28.86 per cent). With boiling water, the bromide hydrolysed to a neutral substance, which separated in thick orange-red prisms from hot benzene or in pale yellow long plates from hot water, m.p. $168-69^{\circ}$. The nature of the product is under investigation.

The sincere thanks of the author are due to Prof P. C. Guha, for his keen interest in the work and to Lady Tata Memorial Trust for the award of a scholarship.

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Received November 4, 1940



STUDIES IN VITAMIN-C OXIDATION. PART I. CO-EXISTENCE OF OXIDISING AND PROTECTIVE FACTORS IN PLANTS FOR VITAMIN-C.

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The existence of a protective factor in vegetables, which protects vitamin-C from oxidation has been established. The enzyme ascorbic acid oxidase and the protective factor occur together in various vegetables, and a method is described for the separation of the two factors from each other. The protective factor inhibits the copper oxidation, while the enzymic oxidation of the vitamin is not influenced by it. The enzyme and the protective factor are more concentrated in the pericarp of the vegetables. The nature and properties of the protective factor have been investigated.

Although vitamin-C is very easily oxidised, particularly in presence of extremely minute amounts of copper, it occurs exclusively in the reduced state in fresh vegetables. It would appear, therefore, that there must be some mechanism in vegetables, which prevents the oxidation of the vitamin. Although the existence of such protective mechanism has been established in animal tissues (De Caro and Giani, *Z. physiol. Chem.*, 1934, **228**, 13; Mawson, *Biochem. J.*, 1935, **29**, 569; Giri, *Biochem. J.*, 1939, **33**, 309; Giri and Shourie, *Indian J. Med. Res.*, 1940, **27**, 685), in plants, however, it has not been shown to be of such wide occurrence.

Since many vegetables contain appreciable amounts of copper, it was of considerable interest to find out whether there exists any protective mechanism which prevents the catalytic oxidation of the vitamin by copper. In the present paper the existence of a protective mechanism for the non-enzymic oxidation of vitamin-C in vegetables is established, and the isolation, nature and properties of the protective constituents form the subject matter of the investigation.

EXPERIMENTAL.

The rate of oxidation of vitamin-C was followed both manometrically and titrimetrically. To each manometric vessel were added to the main chamber: (1) 1 c.c. of *M*/15-phosphate buffer, p_H 5.9, (2) 0.5 c.c. of copper sulphate solution (containing 7 mg. of copper sulphate), (3) 1 c.c. of water or the solution containing the protective factor. The side-bulb contained 0.5 ml. (2 mg.) vitamin-C solution. Potassium hydroxide filter papers

were placed in the central well. Air filled the gas space and the temperature was 30°. The vitamin solution was tipped in when the vessels were placed in the bath and the temperature equilibrium was reached and the oxygen uptake was measured for a 45 minute period. Glass distilled water was used throughout these experiments.

The rate of oxidation of vitamin-C was followed titrimetrically by titrating the vitamin with 2:6-dichlorophenol-indophenol.

Separation of the Protective Factors for Vitamin-C Oxidation free from the Ascorbic Acid Oxidase.

The existence in vegetables of a specific enzyme "Ascorbic acid oxidase" which is responsible for the oxidation of vitamin-C has been established by a number of workers. Chakrabarty and Guha (*Indian J. Med. Res.*, 1937, **24**, 839) have investigated the distribution of the enzyme in various Indian fruits and vegetables, and have shown that the enzyme occurs in various vegetables. It is probable that the effect of the enzyme ascorbic acid oxidase present in vegetables may outweigh the action of the protective constituents present in them, so that the influence of the latter on vitamin-C oxidation may not be apparent, when both of them occur together. Hence it would appear that the failure of previous workers to observe any significant amount of protective substances in vegetables is to be ascribed to the occurrence of ascorbic acid oxidase in association with the protective substances, and without separating the enzyme from the protective constituents, the detection of the latter would not be possible. A method for the separation of the enzyme and the protective constituents from one another is described below.

The expressed juice of the vegetables, cucumber (*Cucumis sativus*), pumpkin (*Cucurbita maxima*), ridge gourd (*Luffa acutangula*), snake gourd (*Tricosanthus anguina*), bitter gourd (*Momordica charantia*), and *Amaranthus* was the starting material for the preparation of the enzyme and the protective factor.

Preparation of an Extract containing the Protective Factors.—To the juice obtained by pressing the pulp of the pericarp of the vegetable, after centrifuging, was added an equal volume of acetone, and the precipitate formed was removed by centrifugation. The clear aqueous-acetone solution was kept on the water-bath, until the solution was completely freed from acetone. This aqueous extract contains the protective substances which inhibit the oxidation of the vitamin both in presence and absence of copper. This will be designated as the protective factor (P. F.) for vitamin-C.

Preparation of the Enzyme.—The precipitate obtained after the addition of acetone contained the enzyme, ascorbic acid oxidase. It was dispersed

in the same volume of water as the original juice, centrifuged to remove the suspended matter, and used for the determination of the activity of the enzyme.

Determination of the Activity of the Enzyme, Ascorbic Acid Oxidase and the Influence of the Protective Factor on Vitamin-C Oxidation.

The reaction mixtures in each case consisted of 5 mg. of ascorbic acid in 20 c.c. of *M*/5-acetic acid-acetate buffer (p_H 5.6). The total volume of the reaction mixture was adjusted to 30 c.c. 2 c.c. of the enzyme and 2 c.c. of the solution containing the protective factor were added to the reaction mixture for determining the activity of the enzyme and the protective action of the acetone extract. The solutions were adjusted to the required p_H before mixing. The controls contained the same amount of vitamin-C without the addition of the protective factor. Immediately after the addition of the vitamin, 2 c.c. samples of each solution were delivered into a series of beakers, each containing 1 c.c. of glacial acetic acid in order to arrest the oxidation, and immediately titrated with the indophenol dye. The volume of the titre, thus obtained, gave the concentration of the vitamin at the beginning of the reaction. At stated intervals of time aliquots were removed and titrated similarly.

Effect of the Protective Factor isolated from Vegetables on the Oxidation of Vitamin-C in the absence of Cu^{++} and of Ascorbic Acid Oxidase.

The results of experiments on the influence of protective factor isolated from various vegetables according to the method described above, on the oxidation of vitamin-C are presented in Table I.

TABLE I
Oxidation of vitamin-C

$p_H = 5.6$. Temp. = 37° . Total volume of the reaction mixture = 30 c.c. (20 c.c. of *M*/5-acetate buffer, V. C. = 5 c.c.; 1 c.c. of P. F.)

Vitamin-C and protective factor from

Time (min.)	V. C. (mg.)	<i>Cucumis sativus.</i>	<i>Cucurbita maxima.</i>	<i>Luffa acu- tangula.</i>	<i>Momordica charantia.</i>	<i>Amaranthus.</i>	<i>Tricosanthes anguina.</i>							
		V. C. oxi- dised.	V. C. oxi- dised.	V. C. oxi- dised.	V. C. oxi- dised.	V. C. oxi- dised.	V. C. oxi- dised.							
0	5.0 mg.	5.0 mg.	5.0 mg.	5.0 mg.	5.0 mg.	5.0 mg.	5.0 mg.							
10	4.11	18%	5.0	0%	5.0	0%	5.0	0%						
15	3.52	30	5.0	0	5.0	0	5.0	0						
20	3.52	30	5.0	0	5.0	0	5.0	0						
30	3.13	38	4.9	2	4.89	4	4.72	6	5.0	0				
60	2.54	50	4.7	6	4.8	4	4.6	8	4.66	8	4.72	6	5.0	0

V. C.=vitamin-C; P. F.=the extract containing the protective factor. Similar results were obtained at the alkaline p_H 7.2.

Effect of the Protective Factor on the Catalytic Oxidation of Vitamin C in presence of added Cu⁺⁺.

(a) *Oxidation followed by Titration.*—The results obtained on the effect of the protective factor obtained from various vegetables, on the oxidation of vitamin-C in presence of added Cu⁺⁺ are presented in Table II.

TABLE II.

Oxidation of vitamin-C.

Temp.=37°; p_H =5.6; Total volume of reaction mixture, 30 c.c. 20 c.c. acetate buffer, 1 c.c. CuSO₄ (0.014 mg. CuSO₄); 5 c.c. V. C. (5 mg.); x c.c. of P. F. ($x=2$ or 5).

Vitamin-C, copper ion and protective factor (P. F.) from

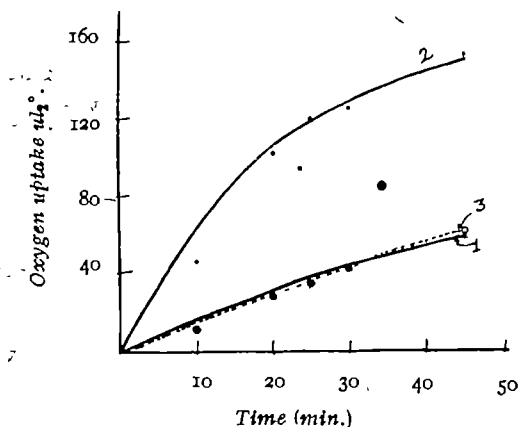
Time (min.)	V. C+Cu		(2 c.c.) <i>C. sativus</i> .		(5 c.c.) <i>C. maxima</i> .		(5 c.c.) <i>M. charantia</i> .		(5 c.c.) <i>T. angulina</i> .	
	V. C.	V. C. oxidis- ed.	V. C.	V. C. oxidis- ed.	V. C.	V. C. oxidis- ed.	V. C.	V. C. oxidis- ed.	V. C.	V. C. oxidis- ed.
0	5.0 mg.		5.0 mg.		5.0 mg.		5.0 mg.		5.0 mg.	
10	2.68	48%	2.97	42%	4.8	6%	4.6	8%	3.96	22%
20	2.11	58	2.59	50	—	—	—	—	—	—
30	1.82	64	2.40	52	4.6	10	4.4	12	2.94	42
60	0.67	88	1.72	66	4.3	14	4.04	20	20.35	54

The results show that the protective factor, prepared from the vegetables, inhibits the catalytic oxidation of the vitamin by added Cu⁺⁺.

(b) *Oxidation followed Manometrically.*—The influence of the protective factor prepared from *Cucumis sativus* on the catalytic oxidation of vitamin-C by Cu⁺⁺ was studied manometrically. The results are shown Fig. 1.

FIG. 1.

Effect of protective factor on the oxidation of vitamin-C by Cu^{++} .



Curves 1—3 refer respectively to vitamin C, vitamin C+ Cu^{++} and vitamin-C+ Cu^{++} +protective factor.

It can be seen from the figure that the oxygen consumption of the system vitamin-C+ Cu^{++} +protective factor is much less than that of vitamin-C+ Cu^{++} system, thereby showing that the factor exerts powerful protection against the catalytic oxidation of the vitamin by Cu^{++} .

Study of the Distribution of the Ascorbic Acid Oxidase and the Protective Factor in Vegetables.

Each vegetable was divided into the following portions:

- (a) The outermost portion (pericarp, representing a layer of about 1/4 cm. thickness from the surface, together with the skin),
- (b) The middle portion (representing the next immediate layer of about 1 cm. thickness), and
- (c) The innermost portion (representing the remaining part of the vegetable, the core)

These different parts of the vegetable were mashed well and the juice expressed separately. The enzyme, ascorbic acid oxidase, and the protective factor were isolated from the juice, and their effect on the oxidation of vitamin-C was determined. The results are presented in Tables IIIA and IIIB.

TABLE IIIA.

Distribution of the enzyme ascorbic acid oxidase in vegetables.

10 C.c. of *M*/5-acetate buffer, 5 mg. of vitamin-C, 1 c.c. of the enzyme solution taken. Total volume = 30 c.c. Temperature = 37°. p_H 5.6.

E_a , E_b and E_c represent the enzyme preparations obtained from pericarp, middle portion and innermost portion respectively, of each vegetable.

Time (min)	<i>C. sativus.</i>				<i>C. maxima.</i>				<i>L. acutangula.</i>				<i>T. angulina</i>			
	%Oxidation of V.C.				%Oxidation of V.C.				%Oxidation of V.C.				%Oxidation of V.C.			
	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.
	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	E_a	E_b	E_c	E_c	E_a	E_b	E_c	E_a	E_b	E_c	E_a	E_b	E_c	E_a	E_b	E_c
10	16	58	28	16	14	52	10	22	20	30	4	20	14	34	—	22
30	34	82	54	38	32	70	24	42	34	42	18	38	28	54	—	40
60	52	96	78	52	42	88	36	68	44	64	18	50	42	74	—	52

TABLE IIIB.

Distribution of the protective factor in vegetables.

Reaction mixture, same as in Table IIIA, with the addition of 1 c.c. of $CuSO_4$ solution (0.014 g. $CuSO_4$) and 1 c.c. of protective factor solution, instead of the enzyme.

P_a , P_b and P_c represent the protective factors isolated from the pericarp, middle portion, and innermost portion respectively, of each vegetable.

Time (min.)	<i>C. sativus.</i>				<i>C. maxima.</i>				<i>L. acutangula.</i>				<i>T. angulina.</i>			
	%Oxidation of V.C.				%Oxidation of V.C.				%Oxidation of V.C.				%Oxidation of V.C.			
	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.	V.C.
	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	P_a	P_b	P_c	P_c	P_a	P_b	P_c	P_a	P_b	P_c	P_a	P_b	P_c	P_a	P_b	P_c
10	46	36	42	30	36	6	6	10	40	12	28	32	40	22	—	28
30	62	50	60	44	52	10	12	18	56	26	42	46	60	42	—	48
60	80	68	76	60	64	14	20	26	74	38	60	66	78	54	—	62

The results show that the enzyme ascorbic acid oxidase is concentrated in the outer skin and the pericarp of the vegetables investigated. The protective factor also is more concentrated in the pericarp than in other portions of the vegetables.

Effect of the Protective Factor on the Enzymic Oxidation of Vitamin-C.

King and co-workers (Stotz, Harrer and King, *Science*, 1937, **86**, 35; *J. Biol. Chem.*, 1937, **119**, 511) have shown that a number of inhibitors of copper catalysis of vitamin-C oxidation, exert similar inhibition of the activity of the enzyme ascorbic acid oxidase, and concluded that the activity of the enzyme is due to the copper present in combination with protein material. Krishnamurthy and Giri (*Indian J. Med. Res.*, 1941 *in press*) have shown recently that pyrophosphate, which inhibits the catalytic oxidation of vitamin-C by Cu^{++} , does not exert the same degree of inhibition on the enzymic oxidation of the vitamin. The question whether the protective factor isolated from the vegetables behaves similarly towards the enzymic oxidation of the vitamin was, therefore, investigated. The results of the experiments on the effect of the protective factor on the enzymic and Cu^{++} oxidation of the vitamin are presented in Table IV.

TABLE IV.

Reaction mixture: 10 c.c. acetate buffer; 1 c.c. of CuSO_4 (0.014 mg. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) or 1 c.c. enzyme; 5 c.c. of the protective factor from *Cucumis sativus*. Total volume = 31 c.c.

Time	%Oxidation of vitamin-C			
	V.C. + Cu	V.C. + Cu + P.F.	V.C. + En.	V.C. + En + P.F.
10 min.	38	20	48	50
30	56	40	72	78
60	74	50	92	96

The results show that the protective factor does not exert any significant degree of protection against the enzymic oxidation of vitamin-C.

DISCUSSION.

The important point that emerges from the results reported in the present investigation is that there are certain constituents in vegetables, which protect vitamin-C from oxidation. These constituents, which are

designated as protective factors for vitamin-C, are widely distributed in vegetables and occur in association with the ascorbic acid oxidase. The two factors—the enzyme which oxidises vitamin-C, and the protective factor which inhibits the oxidation of the vitamin—have been separated from each other and the properties of the protective factor have been investigated.

The protective factor inhibits the non-enzymic oxidation of the vitamin both in presence and absence of added Cu^{++} . Both the enzyme and the protective factor are more concentrated in the pericarp of the vegetables investigated. Although the copper oxidation of the vitamin is inhibited, the enzymic oxidation is not affected to any appreciable extent by the factor.

The Nature of the Protective Factor.—The protective factor is thermostable and dialysable. A concentrated preparation of the factor can be obtained by evaporation on a water-bath, and the concentrated preparation retains the protective property in full.

Further examination of the nature of the constituents (from *Cucumis sativus*, *Cucurbita maxima*, and *Luffa acutangula*) which exert protective action, revealed that one of the important constituents was tartaric acid which exerts protective action on the vitamin. A detailed study of the results obtained on the protective action of tartaric acid and other constituents, which are widely distributed in plants, will be published in the succeeding paper of this series. The extract containing the protective factor gave also tests for reducing sugars. Although the presence of fructose was established by various specific tests, it does not exert any protective action on the vitamin. Further work on the chemical nature of the protective constituents is in progress.

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Received September 9, 1940.

PROPERTIES OF ACTIVATED SUGAR CHARCOAL
COATED WITH VARIOUS ORGANIC SUBSTANCES.
PART III. CATALYTIC DECOMPOSITION OF
HYDROGEN PEROXIDE.

BY HARENDRA KUMAR ACHARYA.

Influence of coats of palmitic acid and α -naphthylamine on activated sugar charcoal on the decomposition of hydrogen peroxide has been studied. Both the coats are equally active and increase the catalytic decomposition of hydrogen peroxide irrespective of acidity or alkalinity of the coats.

In a previous paper (Acharya, *J. Indian Chem. Soc.*, 1937, **14**, 188) the adsorptive properties of activated sugar charcoal, coated with various acidic and alkaline substances, have been reported. In this paper the effect of such coats on the catalytic decomposition of hydrogen peroxide has been studied at 32°.

E X P E R I M E N T A L.

The charcoal used in the following experiment was obtained by activating pure sugar charcoal at 800° for 6 hours.

The coats of palmitic acid and of α -naphthylamine were produced by the method already described (*loc. cit.*). Coats were produced so as to contain 0.05 g. of the substance per g. of charcoal. About 92 to 93% of the coat can be recovered by Soxhlet extraction with alcohol.

To each of 50 c.c. portions of hydrogen peroxide solution (about 3% contained in a cleansed Jena glass bottle 0.5 g. of the following adsorbents were added :

- (i) Activated charcoal,
- (ii) Palmitic acid coated charcoal, and
- (iii) α -Naphthylamine coated charcoal.

A control was also kept. The concentration of hydrogen peroxide was determined by titration against standard potassium permanganate solution and has been given in g. per 100 g. of solution.

R E S U L T S.

TABLE I.

	Control.	Activated charcoal.	Palmitic acid coated charcoal.	α -Naphthylamine coated charcoal.
Initial conc.	2'72	2'72	2'72	2'72
Final conc.				
(i) after 2 hrs.	2'72	2'58	2'49	2'51
(ii) after 24 hrs.	2'72	2'15	1'74	1'80
Millimoles decomposed per g. of charcoal				
(i) after 2 hrs.	—	4'00	6'70	6'20
(ii) after 24 hrs.	—	16'00	28'00	26'50

TABLE II.

Initial conc.	2'82	2'82	2'82	2'82
Final conc.				
after 2 hrs.	2'82	2'73	2'68	2'70
24	2'82	2'41	1'97	1'07
48	2'77	2'18	1'40	1'40
72	2'77	1'72	0'85	0'86
Millimoles decomposed per g. of charcoal				
after 2 hrs.	—	2'50	4'00	3'30
24	—	12'50	24'00	24'00
48	—	20'20	40'2	40'20
72	—	31'00	56'5	56'00

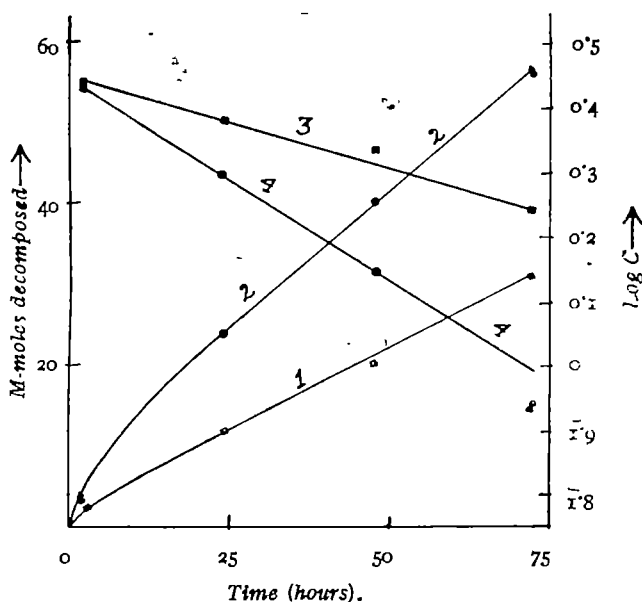
The following results were obtained using 1 g. of charcoal.

TABLE III.

	Control.	Activated charcoal.	Palmitic acid coated charcoal.
Initial conc.	3'09	3'09	3'09
Final conc.			
after 20 hrs.	3'00	2'43	2'11
40	3'07	1'85	1'19
72	1'04	1'46	1'01
Millimoles decomposed per g. of charcoal			
after 20 hrs.	—	19'30	28'8
40	—	35'70	55'0
72	—	57'00	70'2

DISCUSSION.

Tables I, II and III show that both palmitic acid and α -naphthylamine considerably promote the decomposition of H_2O_2 solution by sugar charcoal to the same extent (Table II, curves 1, 2). The promoting effect is greater in dilute solutions and rises during the reaction to a maximum and then diminishes. The decomposition increases with the amount of charcoal employed. The p_H values of conductivity water kept in contact with charcoal coated with palmitic acid and α -naphthylamine for 24 hours are 5.19 and 6.46 respectively (Acharya, *J. Indian Chem. Soc.*, 1936, 13, 723). The fact that both coats have the same effect in spite of the difference in p_H shows that their acidity or alkalinity is of little significance.



Curves 1 and 3 refer to activated charcoal; curves 2 and 4 refer to charcoal coated with palmitic acid or with α -naphthylamine.

In curves 3 and 4, $\log C$ has been plotted against time t where C is the concentration of H_2O_2 at time t kept in contact with the charcoal. The straight line curves indicate that the decomposition of H_2O_2 by activated charcoal and coated charcoal follows a unimolecular reaction rate. But the unimolecular velocity constant k gradually diminishes with time in case of both activated and coated charcoal. Similar diminutions in the values of

k which ultimately become exceedingly small were obtained by Firth and Watson (*J. Chem. Soc.*, 1923, 125, 1750, *cf.* Kepfer and Walton, *J. Phys. Chem.*, 1931, 35, 557) with sugar charcoal. Coated charcoals behave exactly similarly as activated charcoals without coat (Curves 1, 2, 3 and 4). It has been pointed out before that the decomposition increases with the amount of charcoal. It appears therefore that the promoting effect is mainly due to the increase in active surface (*cf.* Acharya, *loc. cit.*).

My best thanks are due to Prof. J. N. Mukherjee for his suggestions and facilities for this work. •

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Received November 6, 1940.

OXALENEDIAMIDOXIME. PART II.

By R. CHATTERJEE.

In continuation of a previous communication, some further work on the nickel complex elucidating its structure is reported. The preparation and properties of different types of complexes of nickel, cobalt, copper and mercury have also been described.

Although a large volume of literature has accumulated on the complex compounds of dimethylglyoxime since the first isolation of the nickel complex by Tschugaeff in 1905, the analogous dioxime $(\text{NH}_2\text{C}=\text{NOH})_2$ appears to have been much less systematically studied in its capacity for complex formation with metals and the nature of the complexes formed. The molecule of oxalenediamidoxime is, however, interestingly constituted from these points of view, in that all the three types of chelation which the molecule may give rise to, form 5 or 6-ring systems and are therefore equally probable, viz. (1) simple co-ordination through two NH_2 groups; (2) replacement of H of NOH and co-ordination through one NH_2 ; (3) inner complexes of Tschugaeff's type in which the amino groups play no part.

Dubsky and Okac (*Coll. Czech. Trav. Chim.*, 1932, **4**, 588), in their studies on the influence of the vicinity of amino group on the formation of complexes of this dioxime, have described the preparation of the previously known nickel complex (Tschugaeff and Surenjanz, *Ber.*, 1907, **40**, 182) and some complexes of copper. Some cobaltous complexes have been described by Schnackig (Dissert., Leipzig Univ., 1938). In furtherance of the work done by these workers, the present author has undertaken a systematic investigation of the complexes of this dioxime with different metals. The anhydrous inner complex of nickel has been described and its usefulness in the direct gravimetric estimation of nickel in presence of other metals has been pointed out in a previous communication (*J. Indian Chem. Soc.*, 1938, **15**, 608). Some further work on the constitution of the nickel inner complex and the preparation of different types of complexes of some more common metals are reported in the present paper.

In analogy with dimethylglyoxime (DH_2) , oxalenediamidoxime $(\text{NH}_2\text{C}=\text{NOH})_2$ is simply written as OxH_2 , indicating the two replaceable hydrogen atoms of the two oxime groups. The following is a brief list of the complexes of Ni, Co, Cu and Hg with oxalenediamidoxime.

	$\text{CoCl}_2 \cdot 2\text{OxH}_2, 6\text{H}_2\text{O}$
$\text{Ni (OxH)}_2, 2\text{H}_2\text{O (T)}$	$\text{CoCl}_2 \cdot 2\text{OxH}_2$
Ni (OxH)_2	$\text{CoCl}_2 \cdot 3\text{OxH}_2 \text{ (S)}$
$\text{Ni (OxH)}_2 \cdot 2\text{CH}_3\text{I}$	$\text{CoCl}_2 \cdot 3\text{OxH}_2 \cdot 2\text{HCl}$
$\text{Ni Cl}_2 \cdot 2\text{OxH}_2$	$\left[\begin{array}{c} \text{Co (OxH)}_2 \\ \text{(NH}_3)_2 \end{array} \right] \text{Cl}$
$\text{Cu (OxH)}_2 \cdot 2\text{H}_2\text{O (D)}$	$\left[\begin{array}{c} \text{Co (OxH)}_2 \\ \text{Py}_2 \end{array} \right] \text{Cl}$
Cu (OxH)_2	$\left[\begin{array}{c} \text{Co (OxH)}_2 \\ \text{(C}_6\text{H}_7\text{N)}_2 \end{array} \right] \text{Cl}$
$\text{CuCl}_2 \cdot \text{OxH}_2$	
$\text{CuCl}_2 \cdot 2\text{OxH}_2$	
$\text{CuSO}_4 \cdot 2\text{OxH}_2$	$\text{Cl} \cdot \text{Hg} \cdot \text{OxH}$

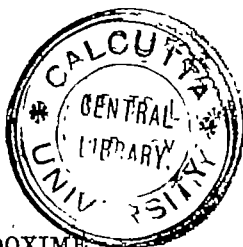
Compounds marked (T), (D) and (S) were prepared by Tschugaeff and Surenjanz (*loc. cit.*), Dubsky and Okac (*loc. cit.*) and Schnackig (*loc. cit.*) respectively. It may be observed that inner complex formation is common in many complexes. The nickel inner complex belongs undoubtedly to Tschugaeff's type, as probably also the brown amorphous copper complex Cu(OxH)_2 . Simple co-ordination compounds are also quite numerous due to ready co-ordination through the amino groups. Chelation of the second type quite probably occurs in the substituted cobaltic complexes, since these are similar to the cobaltamine complexes in general physical properties. The yellow mercuri-complex $\text{Cl} \cdot \text{Hg} \cdot \text{OxH}$ may belong to none of these three types but may simply be a partial salt of the dioxime, only one NOH group entering into combination.

Substitutions at the NH_2 groups are being made in the oxalenediamidoxime molecule, and their effect on complex formation studied.

EXPERIMENTAL.

Nickel bis-oxalenediamidoxime was prepared in the form of light orange, silky needles from a solution of nickel chloride (1 mol.) and oxalenediamidoxime (2 mol.) and rendering the blue coloured solution slightly ammoniacal. The precipitate was well washed with cold water and dried in air. It is insoluble in water and ammonia but soluble in dilute acids. It contains two molecules of water of crystallisation which are readily

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OXALENEDIAMIDOXIME

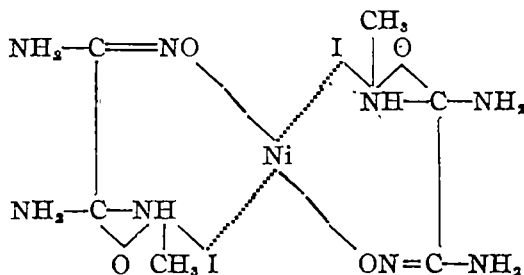
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lost by drying at 110-20° for half an hour. [Found : N, 38.59; Ni, 20.02. Ni (OxH)₂ requires N, 38.3; Ni, 20.04 per cent].

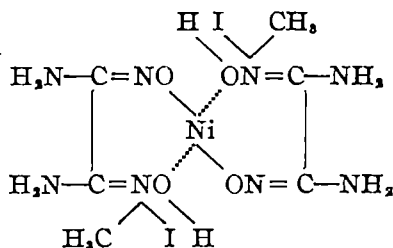
The magnetic susceptibility of the anhydrous substance was examined in a magnetic balance of the Gouy type (mean $H_{4amp} = 5158$ gauss). The substance was diamagnetic ($\chi_p = -0.393 \times 10^{-6}$) indicating a dsp^2 bonding and hence a planar structure of the molecule.

Attempts to methylate the nickel complex with methyl iodide and dimethyl sulphate gave rise to a methiodide with the first reagent but no product with the second under conditions in which Barker (*Chem. News*, 1925, 130, 99) isolated methiodide and methyl sulphate derivatives of nickel dimethylglyoxime.

Assuming Barker's arguments to be correct, the present methiodide must therefore be represented as



or, what appears to the present author more probable, as



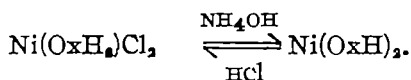
In either formula the difficulty of formation of a doubly linked sulphato derivative is easily apparent. The above experiments in methylation therefore indicate that the nickel dioxime complex is a planar molecule in which the auxiliary linkings through nitrogen (Pfeiffer, *Ber.*, 1930, 63, 1811) appears to occupy *trans* positions.

Nickel bis-oxalenediamidoxime methyl iodide was prepared by heating under reflux a mixture of nickel *bis-oxalenediamidoxime* (1 mol.) and methyl iodide (2 mol.) in alcohol for several days, till the orange suspension went into solution in alcohol giving a green coloration. On slow evaporation at room temperature, pink coloured crystals were deposited. It was washed

several times with CS_2 and then with ether and dried in air. The compound decomposed slowly on keeping, giving inexact analytical results. [Found : N, 20.8; I, 45.5; Ni, 11.7. $\text{Ni}(\text{OxH})_2 \cdot (\text{CH}_3\text{I})_2$ requires N, 19.4; I, 44.0; Ni, 10.2 per cent].

The probable constitution of this compound has already been indicated. An alternative possibility of methylation at the amino groups is ruled out, since such direct methylation has not been found possible with oxalenediamidoxime (Tiemann, *Ber.*, 1889, 22, 2943, 2955).

Nickel bis-oxalenediamidoxime chloride was prepared by adding a solution of oxalenediamidoxime (2 mol.) to an aqueous solution of nickel chloride (1 mol.) when the green colour of the solution changed to dark blue. The solution was kept faintly acid by adding one or two drops of dilute hydrochloric acid and was allowed to crystallise slowly at the ordinary temperature, when transparent blue crystals, highly soluble in water, were deposited. [Found : Cl, 15.1; Ni, 12.2. $\text{Ni}(\text{OxH}_2)_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ requires Cl, 14.99; Ni, 12.4 per cent]. The orange coloured nickel dioxime is precipitated on treatment of the blue solution with ammonia, the change being reversible :



The blue compound is paramagnetic having a magnetic susceptibility approximately equal to a pure nickel salt ($\chi_M = +7.2 \times 10^{-6}$; $\mu = +2.4$ Bohr's magneton). The bonding is therefore sp^3 or simple tetrahedral. The blue colour of the compound is also suggestive of tetrahedral co-ordination.

Cupric bis-oxalenediamidoxime was prepared as a brown precipitate by adding an ammoniacal solution of copper sulphate (1 mol.) to a solution of oxalenediamidoxime (2 mol.) in water. The brown noncrystalline precipitate was washed well with hot water and then dried over sulphuric acid to constant weight. [Found : N, 37.2; Cu, 21.22. $\text{Cu}(\text{OxH})_2$ requires N, 37.66; Cu, 21.36 per cent].

Cupric oxalenediamidoxime chloride was obtained by Dubsky and Okac's method (*loc. cit.*) as a deep green crystalline powder when oxalenediamidoxime (1 mol.) was added to excess of copper chloride (3 mol.) and the solution allowed to evaporate slowly. [Found : N, 22.24; Cl, 27.9; Cu, 25.19. $\text{Cu}(\text{OxH}_2)_2\text{Cl}_2$ requires N, 22.19; Cl, 28.08; Cu, 25.16 per cent].

Cupric bis-oxalenediamidoxime chloride was obtained in deep green, shining crystals by adding a solution of oxalenediamidoxime (2 mol.) to a solution of cupric chloride (1 mol.). The aqueous solution of the compound gives brown coloured precipitate of the inner complex on treatment

with ammonia, the reaction being reversible as in the case of nickel. [Found: N, 30.0; Cl, 18.95; Cu, 17.05. $\text{Cu}(\text{OxH})_2\text{Cl}_2$ requires N, 30.25; Cl, 19.14; Cu, 17.16 per cent].

Cupric bis-oxalenediamidoxime sulphate was obtained in deep green shining scales by partial evaporation of a solution containing copper sulphate (1 mol.) and oxalenediamidoxime (2 mol.). [Found: N, 27.95; Cu, 16.15; SO_4 , 22.92. $\text{Cu}(\text{OxH})_2\text{SO}_4$ requires N, 28.33; Cu, 16.10; SO_4 , 24.28 per cent]. The substance is paramagnetic, ($\chi_e = 2.67 \times 10^{-6}$; $\mu = 1.65$ Bohr's magneton).

Mercuric oxalenediamidoxime monochloride was precipitated in small quantity on mixing aqueous solutions of mercuric chloride (5 g.) and oxalenediamidoxime (4.5 g.) in cold. The yellow precipitate was washed well and dried in air. (Found: Cl, 10.13; Hg, 56.4. ClHgOxH requires Cl, 10.06; Hg, 56.8 per cent).

Cobaltous bis-oxalenediamidoxime chloride hexahydrate was prepared after Schnackig by treating an aqueous solution of cobaltous chloride (1 mol.) with a solution of the dioxime (2 mol.). On slow evaporation, chocolate brown crystals were obtained which lose 6 molecules of water of crystallisation on drying at 110° [Found: N, 23.30; Cl, 14.52; Co, 12.83. $\text{Co}(\text{OxH})_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ requires N, 23.62; Cl, 14.96; Co, 12.44 per cent].

Cobaltous bis-oxalenediamidoxime chloride was obtained as a chocolate brown crystalline powder on treating a warm solution of anhydrous cobaltous chloride (1 mol.) in acetone with an acetone solution of oxalenediamidoxime (2 mol.). The crystals separated almost immediately on mixing the solutions and were found to have identical properties with the dehydrated compound of the previous salt. [Found: N, 30.20; Cl, 19.1; Co, 16.00. $\text{Co}(\text{OxH})_2\text{Cl}_2$ requires N, 30.63; Cl, 19.4; Co, 16.12 per cent].

Diaminodioxalenediamidoxime Cobaltic Chloride.—To an ice-cold solution of cobaltous chloride (1 mol.), well cooled oxalene diamidoxime (2 mol.) solution was added, followed by enough ammonia to make the solution smell of the gas. A rapid current of air was passed through the mixture for about half an hour, filtered and allowed to crystallise in *vacuo*. Brown transparent crystals, soluble in water, readily decomposed by mineral acids. [Found: N, 38.2; Cl, 9.6; Co, 16.54. $(\text{NH}_3)_2\text{Co}(\text{OxH})_2\text{Cl}$ requires N, 38.64; Cl, 9.8; Co, 16.26 per cent].

Dipyridinodi-oxalenediamidoxime Cobaltic Chloride.—Air was passed through an ice-cold solution containing cobaltous chloride (1 mol.), oxalenediamidoxime (2 mol.) and pyridine (2 mol.) for about half an hour. The solution was then filtered and allowed to evaporate slowly in *vacuo*. The product was recrystallised from alcohol. Deep brown, stout needles,

decomposed by dilute acids. [Found : N, 28.83; Cl, 7.1; Co, 12.26. $(C_2H_5N)_2Co(OxH)_2Cl$ requires N, 28.78; Cl, 7.3; Co, 12.12 per cent]. The magnetic susceptibility of the compound was practically nil.

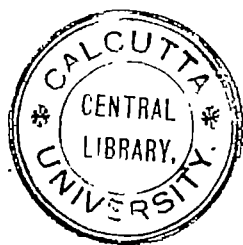
Di-monoethylaminodi-oxalenediamidoxime cobaltic chloride was obtained as brown crystals by passing air for about half an hour through a well cooled solution of cobaltous chloride (1 mol.), dioxime (2 mol.) and a slight excess of 35% ethylamine. [Found : N, 33.23; Cl, 8.31; Co, 14.52. $(C_2H_5NH_2)_2Co(OxH)_2Cl$ requires N, 33.48; Cl, 8.47; Co, 14.41 per cent].

Di-isoquinolinodi-oxalenediamidoxime cobaltic chloride was precipitated as a brown powder by passing air through a well cooled aqueous alcoholic solution of cobaltous chloride (1 mol.), dioxime (2 mol.) and isoquinoline (2 mol.). The compound is similar to the pyridino complex and is decomposed by dilute acids. [Found : N, 23.95; Cl, 5.9; Co, 10.2. $(C_8H_7N)_2Co(OxH)_2Cl$ requires N, 23.88; Cl, 6.05; Co, 10.05 per cent].

The author is indebted to the authorities of St. Joseph's College for providing all laboratory facilities and to Prof. P. Rây for helpful discussions.

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Received September 27, 1940

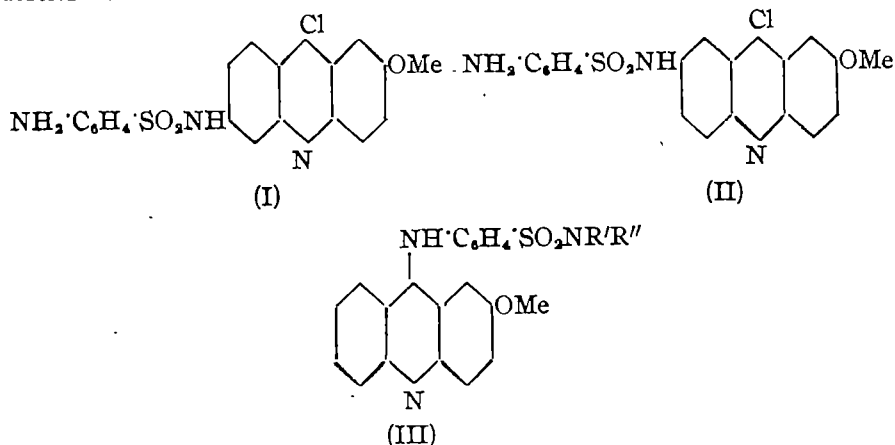


ACRIDINE DERIVATIVES. PART VI.

By S. J. DAS-GUPTA.

Certain sulphanilamido-acridines and acridyl aminobenzenesulphonamide derivatives have been prepared.

In continuation of a previous work (Das-Gupta, *J. Indian Chem. Soc.*, 1939, **16**, 364) where sulphonamidophenylsulphonamidoacridine derivatives have been described, an investigation has now been undertaken to prepare certain simpler acridine derivatives of *p*-aminobenzenesulphonamide where the amide as well as the amino hydrogen of the above compound has been replaced by the acridine nucleus. The interest lies in the fact that such a replacement may increase the therapeutic activity of sulphanilamide (*cf.* Schnitzer and Silberstein, *Z. Hyg. Infek.*, 1929, **109**, 519). In the present paper compounds of the types (I), (II) and (III) have been described.



EXPERIMENTAL.

Hydrochloride of 2-Chloro-4-aminobenzoic Acid.—2-Chloro-4-nitrobenzoic acid (Albert and Linnell, *J. Soc. Chem. Ind.*, 1936, **55**, 54T) was prepared by a modified method in almost theoretical yield. 2-Chloro-4-nitrotoluene (1 g.) was heated in a sealed tube with 5 c.c. of nitric acid (*d* 1.4) at 140-150° for several hours. On cooling the acid was obtained as colourless needles, m.p. 140-41°.

2-Chloro-4-nitrobenzoic acid (1.5 g.) was added gradually to a solution of stannous chloride (15 g.) in fuming hydrochloric acid (15 c.c.), heated on a water-bath. After the addition, heating was continued for further 2 hours. On cooling, the double salt was obtained in a crystalline form. A second crop was obtained on evaporating the mother liquor. After decomposition of the double salt (4 g.) in hot aqueous solution with sulphuretted hydrogen, the evaporation of the filtrate gave the hydrochloride of 2-chloro-4-aminobenzoic acid. Recrystallised from water in colourless needles it had m.p. 187°. (Found: Cl, 33.92. $C_7H_6O_2NCl$, HCl requires Cl, 34.13 per cent). •

Hydrochloride of 2-Chloro-5-aminobenzoic Acid.—2-Chloro-5-nitrobenzoic acid (m.p. 159-61°) was prepared from 2-chloro-5-nitrotoluene in almost theoretical yield by a similar method and was reduced as above. The hydrochloride of 2-chloro-5-aminobenzoic acid was crystallised from water in colourless prismatic needles, m.p. 257°. (Found: Cl, 33.98. $C_7H_6O_2NCl$, HCl requires Cl, 34.13 per cent).

2 - Chloro - 4 - (p - acetylaminobenzene) sulphonamidobenzoic Acid.—Hydrochloride of 2-chloro-4-aminobenzoic acid (1 g.) was treated with sodium carbonate (0.5 g.) and a little water and then *p*-acetylaminobenzenesulphonyl chloride (1 g.) was added and the mixture rubbed in a mortar for about 2 hours. Sodium carbonate was added occasionally to keep the mixture alkaline. The mixture was left overnight and after dilution with water filtered. The filtrate on acidification with hydrochloric acid gave the acid (0.6 g.) as colourless needles from dilute alcohol, m.p. 142°. (Found: N, 7.35. $C_{15}H_{13}O_5N_2ClS$ requires N, 7.60 per cent).

2 - Chloro - 5 - (p - acetylaminobenzene) sulphonamidobenzoic acid was prepared from the hydrochloride of 5-amino-2-chlorobenzoic acid and *p*-acetylaminobenzenesulphonyl chloride exactly in the same way as described above. The acid was crystallised from dilute alcohol in colourless microscopic crystals, m.p. 263°. (Found: N, 7.48. $C_{15}H_{13}O_5N_2ClS$ requires N, 7.60 per cent).

4 - (p - Acetylaminobenzene) sulphonamido- 4' - methoxydiphenylamine 2 - carboxylic Acid.—4 - (*p* - Acetylaminobenzene) sulphonamido - 2 - chlorobenzoic acid (1 mol.), *p*-anisidine (1 mol.) and anhydrous potassium carbonate (1 mol.) were refluxed together in amyl alcoholic solution with little copper powder for several hours. The mixture after dilution with water was distilled in steam to remove amyl alcohol. On filtration of the residual liquid and acidification with hydrochloric acid in cold, the diphenylamine was precipitated and was crystallised from dilute alcohol (charcoal) in almost colourless microscopic needles, m.p. 158-60°. It gave the usual

test of diphenylamine. (Found: N, 8.97. $C_{22}H_{21}O_6N_3S$ requires N, 9.23 per cent).

5 - (p-Acetylaminobenzene)sulphonamido-4-methoxydiphenylamine-2-carboxylic acid was prepared from 5-(p-acetylaminobenzene)sulphonamido-2-chlorobenzoic acid and p-anisidine in the same way as in the previous case, in almost colourless needles from dilute alcohol (charcoal), m.p. 218-20°. (Found: N, 9.1. $C_{22}H_{21}O_6N_3S$ requires N, 9.23 per cent).

2-(4'-Acetylaminobenzene)sulphonamido-7-methoxy-5-chloroacridine (structure analogous to I).—The 4-(p-acetylaminobenzene)sulphonamido-4-methoxydiphenylamine-2-carboxylic acid was refluxed with excess of phosphorus oxychloride on a water-bath for more than one hour. Excess of oxychloride was removed in vacuum. The residual mass was treated with ice-cold water and made just alkaline with ammonia. The chloroacridine was collected, washed with water and crystallised from a mixture of acetone and water (1:2) in reddish microscopic crystals, m.p. 245-47° (decomp.). It gives fluorescence in dilute solutions in acetone, alcohol and benzene, and is soluble in both acids and alkalis. (Found: N, 9.24; Cl, 7.61. $C_{22}H_{18}O_4N_3ClS$ requires N, 9.22; Cl, 7.79 per cent).

3-(4'-Acetylaminobenzene)sulphonamido-7-methoxy-5-chloroacridine (structure analogous to II) was prepared from 5-(p-acetylaminobenzene)sulphonamido-4'-methoxydiphenylamine-2-carboxylic acid in the same manner as described above and crystallised from a mixture of acetone and water in orange microscopic crystals, m.p. 243-44° (decomp.). It gives fluorescence in dilute solutions in alcohol, acetone and benzene. (Found: N, 8.89. $C_{22}H_{18}O_4N_3ClS$ requires N, 9.22 per cent).

3-(4'-Aminobenzene)sulphonamido-7-methoxy-5-chloroacridine.—3-(p-Acetylaminobenzene)sulphonamido-7-methoxy-5-chloroacridine (0.5 g.) was hydrolysed by heating with 12 c.c. of aqueous alcoholic hydrochloric acid (5%) for 20 minutes when a clear solution was obtained. After cooling and diluting with little water, the solution was neutralised with ammonia when a solid separated. It was filtered, washed with water and crystallised from dilute alcohol in reddish needles, melting indefinitely at ca 180°. It gives fluorescence in dilute solutions and also responds to diazo reactions. (Found: N, 10.39; Cl, 8.37. $C_{20}H_{16}O_3N_3ClS$ requires N, 10.16; Cl, 8.58 per cent).

N⁴-(2-Chloro-7-methoxy)-acridylaminobenzenesulphonamide (structure analogous to II).—Equimolecular quantities of 7-methoxy-2,5-dichloroacridine and p-aminobenzenesulphonamide were heated in phenol at 110-120° for 2 hours. After cooling the mixture was poured into dilute sodium hydroxide solution, filtered and washed. The solid collected was crystallised from a large volume of alcohol in small yellow needles, m.p. 286°. (Found: N, 9.9. $C_{20}H_{16}O_3N_3ClS$ requires N, 10.16 per cent). The com-

pound is slightly soluble in acids but insoluble in alkalis. It gives fluorescence in dilute alcoholic solutions.

N^4 -(2-Chloro-7-methoxy)acridylaminobenzenesulphondiethylamide.—Equimolecular quantities of 7-methoxy-2;5-dichloroacridine and *p*-aminobenzenesulphondiethylamide were heated in phenol at about 120° for 2 hours. The mixture was poured into dilute sodium hydroxide solution when a semi-solid mass separated, which was washed with cold water and crystallised from ether in orange-yellow needles, m.p. 175° . (Found: N, 8.67. $C_{24}H_{24}O_3N_3ClS$ requires N, 8.94 per cent). By passing dry hydrogen chloride through an ethereal solution of this compound the hydrochloride separated which was crystallised from alcohol-ether mixture in small deep orange needles, m.p. $260-61^\circ$. The base as well as the hydrochloride give fluorescence in dilute alcoholic solutions.

N^4 -(7-Methoxy)-acridylaminobenzenesulphondiethylamide.—Equimolecular quantities of 7-methoxy-5-chloroacridine and *p*-aminobenzenesulphondiethylamide were heated in phenol at $120-130^\circ$ for 2 hours. After pouring the mixture into cold dilute sodium hydroxide solution, a semi-solid mass separated, which after treatment with ether solidified. It was obtained as yellow microscopic crystals from alcohol and water (1:1), m.p. $263-64^\circ$. It is insoluble in alkalis but soluble in acids and gives fluorescence in dilute alcoholic solutions. (Found: N, 9.28. $C_{23}H_{22}O_3N_3ClS$ requires N, 9.55 per cent).

N^4 -(2-Chloro-7-methoxy)-acridylaminobenzenesulphonacetamide.—Equimolecular quantities of 7-methoxy-2:5-dichloroacridine and *p*-aminobenzenesulphonacetamide (m.p. 182°) were heated in phenol at $150-160^\circ$ for 3 hours. After pouring into ice-cold dilute sodium hydroxide solution a semi-solid mass was obtained. This was washed with water and then treated with ether when a solid was obtained. Orange microscopic crystals separated from a large volume of alcohol and water (1:1), m.p. $248-50^\circ$. It is soluble in dilute acids and alkalis. (Found: N, 8.95. $C_{22}H_{18}O_4N_3ClS$ requires N, 9.22 per cent).

N^4 -(7-Methoxy)acridylaminobenzenesulphonacetamide was prepared from 7-methoxy-5-chloroacridine and *p*-aminobenzenesulphonacetamide in the same manner as in the previous case. Orange microscopic crystals were obtained from alcohol and water (1:1), m.p. $143-45^\circ$. The compound is soluble in water, more in alkalis and acids. (Found: N, 9.51. $C_{21}H_{16}O_3N_3ClS$ requires N, 9.87 per cent).

The author wishes to express his sincere thanks to Dr. U. P. Basu for his kind interest in this investigation.

THE AZO COMPOUNDS FROM MORPHINE. PART I.

BY AMARESH CHANDRA ROY.

Morphine has been coupled with various diazotised amines to produce azo-dyestuffs. It has been found that the pharmacological activity of morphine becomes modified but is not destroyed.

The coupling of morphine with a diazonium salt to produce an azo-dyestuff was first studied by Wieland and Kappelmeir (*Annalen*, 1911, **383**, 336), who prepared phenylazomorphine from diazobenzene chloride and a solution of morphine in alkali. Later on Lautenschlager (*Arch. Pharm.*, 1919, **257**, 13) tried to prepare azo compounds of morphine, emetine, sparteine, physostigmine, piperidine, conine, and nicotine by coupling these alkaloids with diazotised arsanilic acid, diazobenzenesulphonic acid, 2:5-dichlorobenzenediazonium chloride etc. in alkaline solution and found that morphine was the only alkaloid of opium which gave an azo-dye but the physiological action of the former was destroyed by its conversion into diazonium compound. Recently Charrier and Neri (*Gazzetta*, 1929, **59**, 804) prepared 2-phenylazomorphine and studied its transformation into 2-phenyl-azoapomorphine by the action of concentrated sulphuric acid.

The present work is undertaken with a view to study the effect of substitution by diazo and substituted diazo groups on the pharmacological activity of morphine and also to prepare azo-dyestuffs showing optical activity.

The following aromatic amino compounds have been diazotised and coupled with morphine in alkaline solution and the corresponding azo-dyestuff obtained: aniline, *p*-toluidine, 2:4-xylydine, *p*-chloroaniline, 2:4:6-tribromoaniline, *p*-aminophenol, *o*-anisidine, *o*-, *m*-, and *p*-nitroaniline, benzidine and α -naphthylamine. The azo compounds, thus prepared, are coloured substances of shades varying from orange-red to deep brown.

All these compounds show distinct hypnotic and analgesic action like morphine. They have practically no effect on paramoecia even in a concentration of 1 in 100 and are less toxic and less depressant than morphine. They have distinct action on the central nervous system but develop no convulsion and exaggeration of reflexes. The compounds have practically no action on the heart and in lower concentrations increase the tone and amplitude of contractions of the isolated intestine. Thus it appears that the pharmacological activity of morphine is not altogether destroyed, as was previously observed by Lautenschlager (*loc. cit.*).

The optical rotatory properties could not be determined owing to the intense colour of the compounds in caustic alkalis. Concentrated solutions of the compounds in alcohol and other solvents were also tried but no appreciable rotation could be observed owing probably to the small concentration of the azo-dyes in the solutions.

EXPERIMENTAL.

Phenylazomorphine.—Diazobenzene chloride, prepared from aniline (4.6 g.), concentrated hydrochloric acid (23 g.) and sodium nitrite (3.5 g.), was gradually added, during the course of half an hour, with constant stirring to a freshly prepared cooled solution of morphine (15 g.) in sodium hydroxide. The dark red liquid was allowed to stand overnight at the room temperature, filtered from the resinous matter and on neutralisation with dilute hydrochloric acid, gave a brown amorphous powder which was filtered and washed with water. The compound, thus obtained, was redissolved in *N*-sodium hydroxide and reprecipitated by neutralising with *N*-hydrochloric acid; this process was repeated twice and the precipitate was ultimately filtered, washed with water and dried in a steam-oven. From dilute ethyl alcohol it crystallised in orange-yellow needles, m.p. 175° (decomp.), and was identical with 2-phenylazomorphine, prepared by Wieland and Kappelmeyer (*loc. cit.*).

All other compounds were prepared in the same way as the phenylazomorphine by taking equimolecular quantities of the amino compounds and morphine. For the final purification, the compounds were dissolved in anhydrous methyl alcohol, the solution clarified with animal charcoal, filtered and was concentrated; the dystuffs were reprecipitated from this solution by adding an excess of ether, filtered and dried. The results are summarised in Table I.

With the exception of phenylazomorphine, which crystallises from ethyl alcohol in orange-yellow needles, all other compounds are amorphous powders which do not crystallise from any solvent. The yield of the crude products in all cases is 30-35% of that required by theory because of resin formations. All these compounds are sparingly soluble in water, petroleum ether, ether and chloroform but soluble in methyl and ethyl alcohols, glacial acetic acid and pyridine. They are slightly soluble in concentrated ammonia but dissolve freely in dilute alkali hydroxide from which they can be precipitated by neutralisation with dilute mineral acids or by passing a current of carbon dioxide. In dilute mineral acids all of them dissolve, though sparingly, with an orange-yellow colour. They

TABLE I.

 (M stands for the azomorphine group $C_{17}H_{18}O_5-N-N=N-$ in the formulæ).

Name of the compound.	Formula.	Appearance on purification.	M. p.	Colour in conc. H_2SO_4 .	Colour in NaOH.	Colour with Erdmann's reagent.	Colour with Froede's reagent.	Analysis. Found.	Calc.
Phenylazo-morphine	$M-C_6H_5$	Orange-yellow needles	175° (decomp.)	Red	Deep red	Brown	Red	N, 10.51	10.79
<i>p</i> -Tolylazo-morphine	$M-C_6H_4CH_3$	Orange amorphous powder	210° (decomp.)	"	"	"	"	N, 10.08 C, 70.98 H, 5.9	10.42 71.46 6.4
2:4-Dimethylphenylazo-morphine	$M-C_6H_3(CH_3)_2$	Orange-red powder	Does not fuse at 300°	"	"	"	Blood-red	N, 9.67 C, 71.60 H, 6.2	10.07 71.94 6.47
<i>p</i> -Chlorophenylazomorphine	$M-C_6H_4Cl$	Maroon-red powder	"	"	"	Yellow changing to brown	Chocolate	N, 9.48	9.91
2:4 6-Tribromophenylazo-morphine	$M-C_6H_2Br_3$	Deep red powder	"	Dark red	"	"	Deep "	N, 6.3	6.71
<i>p</i> -Hydroxyphenylazo-morphine	$M-C_6H_4OH$	Dark brown powder	"	Dirty pink	Reddish brown	Reddish brown	Dirty pink	N, 9.92	10.37
<i>o</i> -Methoxyphenylazo-morphine	$M-C_6H_4OCH_3$	Chocolate powder	"	"	Orange	Deep brown	Pink changing to red	N, 9.85	10.02
<i>o</i> -Nitrophenylazomorphine	$M-C_6H_4NO_2$	Light brown powder	"	Brown	Bright red	Brown changing to yellow	Brown changing to yellow	N, 9.35 C, 63.15 H, 4.93	9.67 63.59 5.07
<i>m</i> -Nitrophenylazomorphine	$M-C_6H_4NO_2$	Dark brown powder	"	Yellowish brown	Blood-red	Orange	"	N, 9.28	9.67
<i>p</i> -Nitrophenylazomorphine	$M-C_6H_4NO_2$	"	"	Brown	Red	Orange	Deep brown	N, 9.41	9.67
Benzidine-tetrazo-morphine	$M-C_6H_4C_6H_4N_4$	Dark chocolate powder	"	Magenta	Deep red	Brown changing to orange	Violet-red	N, 10.67	10.82
α -Naphthylazomorphine	$M-C_{10}H_7$	Reddish brown powder	"	Violet	"	"	Violet	N, 9.64	9.56

dissolve in cold concentrated sulphuric acid giving deeply coloured solutions of varying shades, depending upon the nature of the substituents, which become yellow on dilution with water giving precipitates of the original dyestuff, but a prolonged treatment with concentrated sulphuric acid at the ordinary temperature changes them probably into apo-compounds (*cf.* Charrier and Neri, *loc. cit.*) The hydrochloric acid solutions of the compounds give with a solution of ferric chloride greenish yellow colouration which changed to deep yellow on boiling in all cases. With concentrated nitric acid all these compounds give yellow colourations which become almost colourless on warming owing to decomposition. They do not reduce ammoniacal silver nitrate solution and give colour reactions entirely different from morphine with Erdmann's and Froede's reagents. For the pharmacological work the compounds are dissolved in the minimum amount of sodium hydroxide and the sodium salts, thus formed, are precipitated with an excess of alcohol, filtered, dried and used for the investigation.

Further work on the pharmacological action of these compounds is in progress.

My best thanks are due to Dr. P. C. Ray, Professor of Pharmacology, Prince of Wales Medical College, Patna, for giving me facilities to work in his laboratory.

B. N. COLLEGE, PATNA.

Received April 27, 1940.

THE ALKALOIDS OF *RAUWOLFIA CANESCENS*, LINN. PART I.

BY (MISS) ASIMA MOOKERJEE.

An alkaloid Rauwolscline ($C_{21}H_{26}O_3N_2$, m.p. $231-32^\circ$) has been isolated from *Rauwolfia canescens*. Its physical and chemical properties have been studied and a number of salts and derivatives prepared. The colour reactions of rauwolscline show it to be quite different from other Rauwolfia alkaloids but similar to yohimbine. Rauwolsclenic acid has been obtained from the alkaloid presumably by the hydrolysis of a CO_2Me group in rauwolscline; the acid has been reconverted into the alkaloid.

Although *Rauwolfia serpentina*, Benth. (N.O. *Apocynaceae*) has been the subject of a number of investigations (Siddiqui and Siddiqui, *J. Indian Chem. Soc.*, 1931, **8**, 667; 1932, **9**, 539; 1935, **12**, 37; 1939, **16**, 421; Van Itallie and Steenhauer, *Arch. Pharm.*, 1932, **270**, 313), other species of *Rauwolfia* do not appear to have received much attention. Greshoff (*Ber.*, 1890, **28**, 3537) reported the presence of an alkaloid (0.4%) in the bark of *Rauwolfia canescens*, but he did not purify his base or determine its molecular formula and properties. Recently Koepfli (*J. Amer. Chem. Soc.*, 1932, **54**, 2412) reported the isolation of a crystalline alkaloid, rauwolfine, $C_{20}H_{26}O_3N_2$, m.p. $235-38^\circ$ (decomp), from an African species, namely *R. caffra*.

The present communication deals with the isolation and examination of an alkaloid from *R. canescens*, known locally as "Barachándá." It is a small shrub inhabiting the moist and hot regions of India. Its roots are sometimes used to adulterate those of *R. serpentina*. The alkaloid appears to be different from any of the Rauwolfia alkaloids, so far described, and has consequently been named *Rauwolscline*.

Rauwolscline is distributed throughout the plant. Root-bark contains 0.1%, stem-bark 0.2% and leaves 0.5 % of pure rauwolscline, besides other bases, an account of which will be given in a subsequent communication.

Rauwolscline forms thick, pale yellow plates, m.p. $231-32^\circ$ (decomp.)* having $[\alpha]_D^{30} = -40^\circ$ (alcohol). The analytical data of the base, as also of a number of salts derived therefrom, indicate the formula $C_{21}H_{26}O_3N_2$ which is further supported by the M.W. data. It is devoid of *N*-methyl and methylenedioxy groups, but the presence of one methoxy group has been established. The base does not give any colouration with ferric chloride.

* The melting points recorded in this paper, are uncorrected.

It is faintly alkaline to litmus and possesses a very bitter taste, which is also shared by its salts. The salts of the monacidic base are generally well-crystalline. The hydrochloride and nitrate are neutral, while the sulphate and oxalate show an acid reaction towards litmus. The picrate is orange, while the chloroplatinate is amorphous and pale orange in colour.

Rauwolscine gives characteristic colour reactions with concentrated sulphuric acid and other alkaloidal reagents, as shown below.

TABLE I.

Reagent.	Colour.
H_2SO_4 (conc)	Blue with a violet tinge changing to red.
Conc. $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$	Deep blue changing to green
Fröhde's reagent	Navy blue, then purple and finally yellow.
Erdmann's reagent	Bluish green, gradually changing to yellow
Mandelin's reagent	Blue, changing to yellow.

Precipitates are formed from the hydrochloride with many reagents, such as phosphomolybdic acid (greenish white), iodine in potassium iodide (reddish yellow, 1 in 1000 dilution), potassium mercuri-iodide (white), potassium bismuth iodide (orange-red). Of these the last named compound can produce a precipitate in a dilution of 1 in 200,000.

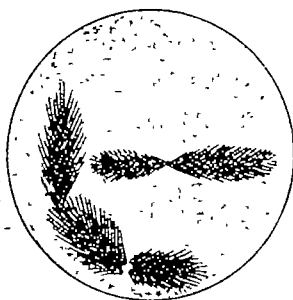
The analytical data as also the colour reactions are, therefore, different from those of the other Rauwolfia alkaloids. Rauwolscine, however, shows a considerable amount of similarity in properties and colour reactions with yohimbine. This is illustrated in the following table.

TABLE II.

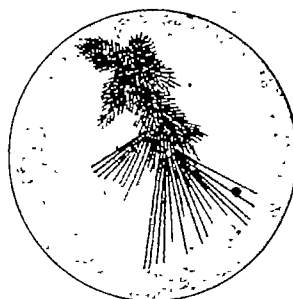
Comparison between yohimbine and rauwolscine.

Reagent.	Yohimbine.	Rauwolscine.
Conc. H_2SO_4	Blue with a violet tinge	Same
Conc. $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$	Deep blue with violet tinge changing to green.	Same
Conc. HNO_3	Yellow.	Same
Fröhde's reagent	Navy blue, then yellow.	Same
Erdmann's reagent	Greenish blue, then green, finally yellow	Same
Mandelin's reagent	Deep blue, then reddish yellow.	Same
Specific rotation		
Free base	+ 56° (alcohol)	- 40° (alcohol)
Hydrochloride	+ 105° (water)	+ 74° (water)
Melting point		
Free base	234° (decomp.)	231-32° (decomp.)
Hydrochloride	295-300° (decomp.)	278-80° (decomp.)
Crystalline form and colour	Colourless needles.	Pale yellow thick plates.

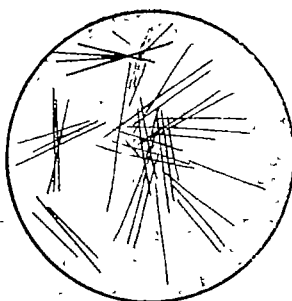
Rauwolscine oxalate.



Rauwolscine oxalate.



Rauwolscine.



Rauwolscine nitrate



Rauwolscine hydrochloride.

Melting point depression was observed when the two bases as also their hydrochlorides were mixed together showing that they are different. The physical properties of the base, rauwolscine are also different from

other alkaloids of the yohimbine group having the same molecular composition.

Although rauwolscine is precipitated from an aqueous solution of its salts by means of ammonia, prolonged contact with concentrated ammonia or aqueous potassium hydroxide converts rauwolscine into a water-soluble compound, m.p. $262-64^{\circ}$ (decomp.). This substance is neutral to litmus, but is more soluble in dilute sodium bicarbonate solution than in the same volume of water. It is also soluble in moderately strong ammonium hydroxide. The ferric test is negative. Apparently the transformation product contains a CO_2H group and has consequently been named rauwolscinic acid, which shows absence of methoxy group by Zeisel's method. The assumption is, therefore, made that rauwolscinic acid is formed from rauwolscine by the hydrolysis of a CO_2Me group. Rauwolscinic acid could be reconverted into rauwolscine by the action of methyl alcohol and hydrogen chloride. These observations prove the presence of a CO_2Me group, which has so far not been detected in other *Rauwolfia* alkaloids, but which is present in yohimbine and some other alkaloids.

It is presumed, therefore, that although rauwolscine and yohimbine are not identical, the main features of the structures of the two alkaloids may be very similar.

The pharmacological action of rauwolscine, as also further work on the constitution of the alkaloid, is in progress.

EXPERIMENTAL.

Isolation of Rauwolscine.—*Rauwolfia canescens* were collected from the District of Howrah (Bengal) and were identified by Prof. A. Das-Gupta of Bangabasi College, Calcutta, to whom the author offers her best thanks. 2 Kg. of air-dried leaves were percolated thrice with rectified spirit (50 litres) containing 0.1% acetic acid at room temperature. The combined bright green extracts were concentrated to about 800 c.c. on the water-bath under reduced pressure. The dark green viscous liquid was poured into cold water (600 c.c.) in a thin stream with constant stirring and allowed to stand. Resinous matters which had separated out were then filtered off and the aqueous filtrate was thrice shaken up with ether (200 c.c. each time) to remove oily and other impurities. The red aqueous solution was then covered with ether (300 c.c.), made just basic by the addition of concentrated ammonia, and the liberated base taken up in ether. The aqueous solution was shaken up three times with ether (300 c.c. each time) till a test portion on removal

of ether and acidification with hydrochloric acid failed to give any appreciable amount of precipitate with potassium bismuth iodide. The aqueous solution showed the presence of not inconsiderable amount of alkaloids as tested by Dragendorff's reagent. Efforts are being made to isolate the water-soluble alkaloids.

The combined ethereal extracts were washed with water, dried over sodium sulphate and concentrated to about 250 c.c. A solution of anhydrous oxalic acid in ether was then gradually added to the above extract till no further precipitation was observed. The crude oxalate of rauwolscine, thus obtained, was collected, washed with ether, and then heated with absolute alcohol on the water-bath for three hours to dissolve gummy substances and colouring matters, cooled, filtered and washed with absolute alcohol; yield 13 g. Further purified by two or three crystallisations from hot water, rauwolscine oxalate formed clusters of silky radiating colourless needles, m.p. 245-46° (decomp.). It is acidic to litmus and liberates iodine from a mixture of aqueous potassium iodide and potassium iodate. Rauwolscine oxalate has two molecules of water of crystallisation which are completely removed on drying in *vacuo* over P_2O_5 for 3 hours at 125-30°. (Found in dry specimens: N, 6.27; OMe, 7.1. $C_{21}H_{26}O_3N_2 \cdot H_2C_2O_4$ requires N, 6.3; OMe, 6.98 per cent).

To prepare the free base, the oxalate (3 g.) was dissolved in warm water (400 c.c.), cooled and made just alkaline with ammonia. The cream-coloured needles were collected, washed with water and dried in a desiccator over calcium chloride. Two or three crystallisations from benzene gave pure rauwolscine, m.p. 231-32° (decomp.), not raised by further crystallisations; yield 2 g. It has $[\alpha]_D^{30} = -40^\circ$ (0.266 g. of substance in alcohol, $l = 50$ mm.). No significant loss in weight occurred on drying in *vacuo* over P_2O_5 for 3 hours at 120-25°. (Found: C, 71.5; H, 7.5; N, 8.1; OMe, 8.52 per cent). Another specimen crystallised from alcohol and dried at 140-45° in *vacuo* over P_2O_5 for 2 hours was also analysed [Found: C, 71.2; H, 7.6; OMe, 8.5. M.W. (titration), 355.8, 355. $C_{21}H_{26}O_3N_2$ requires C, 71.2; H, 7.3; N, 7.91; OMe, 8.76 per cent. M.W., 354).

Rauwolscine is freely soluble in ether, ethyl acetate, chloroform, and hot alcohol, less soluble in benzene, and very sparingly soluble in petroleum ether and water.

Rauwolscine hydrochloride was obtained by dissolving the base in the minimum quantity of hot 2N-acid. The colourless prismatic needles of the *hydrochloride* obtained on cooling the solution were recrystallised from hot water, m.p. 278-80° (decomp.). It has $[\alpha]_D^{30} = +74^\circ$ (0.2750 g. of substance in 25 c.c. of water, $l = 50$ mm.). The salt is neutral to

litmus and suffered no loss in weight on drying at 140° for 2 hours in *vacuo* over P_2O_5 . (Found : Cl, 9.09. $C_{21}H_{28}O_3N_2, HCl$ requires Cl, 9.09 per cent.)

Rauwolscine nitrate, obtained in a similar manner, is also neutral to litmus, but is less soluble in water than the hydrochloride, m.p. $257-58^{\circ}$ (decomp.). The salt also appears to be free from water of crystallisation. (Found in specimen dried at $130-35^{\circ}$ for 2 hours in *vacuo* over P_2O_5 ; N, 9.85. $C_{21}H_{28}O_3N_2, HNO_3$ requires N, 10.0 per cent.)

Rauwolscine Sulphate.—The precipitated base was dissolved in a slight excess of 2*N*-sulphuric acid and the solution almost evaporated to dryness. The cooled residue was washed with cold absolute alcohol and crystallised from the same solvent, when colourless needles, m.p. $256-57^{\circ}$ (decomp.), were obtained. It is more soluble in water than the hydrochloride and unlike the hydrochloride showed acidic reaction towards litmus. (Found in specimen crystallised from water and dried at $110-15^{\circ}$ for 2 hours in *vacuo* over P_2O_5 ; S, 7.02. $C_{21}H_{28}O_3N_2, H_2SO_4$ requires S, 7.08 per cent.)

Rauwolscine Chloroplatinate.—An amorphous orange-yellow precipitate was obtained on adding an excess of 5% chloroplatinic acid to a concentrated solution of the hydrochloride in water. It was washed with hot water and dried at $115-20^{\circ}$ for 3 hours in *vacuo* over P_2O_5 . m.p. $255-57^{\circ}$ (decomp.). (Found : Pt, 16.72. $C_{21}H_{28}O_3N_2, H_2PtCl_6$ requires Pt, 17.53 per cent). Attempts to crystallise the compound from a large volume of alcohol resulted in the formation of the hydrochloride and other amorphous products. Rauwolscine chloroplatinate is insoluble in acetone.

Rauwolscine picrate was obtained as an orange precipitate on treating an ethereal solution of the base with ethereal picric acid. Crystallised from alcohol it formed shining orange plates, m.p. 208° (decomp.). [Found in specimens dried for 2 hours at 110° in *vacuo* over P_2O_5 ; C, 54.6; H, 6.7; N, 10.2, 10.3. $C_{21}H_{28}O_3N_2, C_6H_2(NO_2)_3OH, 2C_2H_5OH$ requires C, 55.1; H, 6.1; N, 10.37 per cent).

Rauwolscinic Acid.—Finely divided rauwolscine (0.1 g.) was covered with ammonia (30 c.c., d 0.88) and allowed to stand at room temperature in a closed vessel. The base passed into complete solution in course of a week. The clear pale yellow solution was evaporated on the water-bath to a small volume, acidified with *N*/2-acetic acid and then completely evaporated to dryness. The brown residue was washed with a small quantity of cold water and crystallised thrice from hot water, when pale brown prisms, m.p. $262-64^{\circ}$ (decomp.) were obtained. The product was neutral to litmus but dissolved in sodium bicarbonate solution and dilute acids in the cold. It has a slightly bitter taste. Rauwolscinic acid has one

molecule of water of crystallisation which is lost on drying in *vacuo* over P_2O_5 for 4 hours at $120-25^\circ$. (Found in a dry specimen : N, 8.23. $C_{20}H_{24}O_3N_x$ requires N, 8.23 per cent). A methoxy estimation proved the absence of methoxy groups. This acid is being further investigated.

Rauwolsine from Rauwolscinic Acid.—A stream of dry hydrogen chloride was passed through rauwolscinic acid (0.1 g.), suspended in methyl alcohol (5 c.c.), till saturated. The acid passed into solution and the clear solution on standing overnight deposited colourless, shining needles of rauwolsine hydrochloride. These were collected and washed with cold methyl alcohol, m.p. $276-78^\circ$ (decomp.).

To prepare the free base, the hydrochloride was dissolved in warm water (20 c.c.), the solution cooled and made just alkaline with dilute ammonia. The cream-coloured needles which separated out, were collected, washed with water, crystallised from dilute alcohol and finally from benzene. Pale yellow plates (0.09 g.), m.p. $230-31^\circ$ (decomp.), were obtained. The product did not depress the m.p. of rauwolsine, when mixed together.

Photomicrographs of rauwolsine and some of its salts are reproduced on p. 35.

In conclusion the author desires to offer her best thanks to the authorities of the University of Calcutta for the grant of a scholarship which has enabled her to take part in this investigation. Her best thanks are also due to Dr. P.K. Bose for his keen interest and for the facilities given, and to Mr. N. Ghosh, M.Sc., for the micro-analytical results recorded in this paper.

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Received September 27, 1940.

THE INFLUENCE OF LIGHT ON NITROGEN FIXATION IN DACCA SOIL.

BY M. SULAIMAN.

Experiments have been made with Dacca soil with an organic carbon content of 365 mg per 100 g. of soil according to conditions as laid down by Dhar for the fixation of nitrogen in presence of carbohydrates.

In recent years Dhar ("Presidential Address of the National Academy of Sciences, India," Jan., 1937; Dhar and Mukerji, *J. Indian Chem. Soc.*, 1938, **15**, 543) has put forward the view that nitrification in soils and nitrogen fixation from the atmosphere are, especially in the tropics, photochemical, at least so far as bacterial action goes. This postulation, if established, will open a new chapter at least so far as the tropical countries are concerned. According to Dhar, substances rich in carbohydrates like butter, ghee (clarified butter), sodium tartrate, citrate, oleate, palmitate, stearate, canesugar, glycerol, molasses, etc., when mixed with soil and exposed to air and light are oxidised on the soil surface and causes nitrogen fixation. It was felt desirable to examine as to how far the influence of light causes nitrogen fixation in Dacca soil in presence of carbohydrates. Canesugar was chosen as the carbohydrate in this investigation. The Dacca soil which was selected for experiments on nitrogen fixation, had an organic carbon content of 365 mg. per 100 g. of soil and the pH of the soil was 5.2. The total nitrogen content of the soil was 48 mg. per 100 g. of oven-dry soil. The same sample was used throughout. It was found by experiment that the soil did not contain any *azotobacter*.

EXPERIMENTAL.

600 G. of soil were thoroughly mixed with 12 g. of canesugar separately in two dishes. One of the dishes with its contents was exposed to ordinary sunlight daily for eight hours, whilst the other was wrapped round with black cloth to exclude light and kept outside along with the exposed one to eliminate the temperature factor. The moisture was made up to 20% at the beginning to mix the ingredients properly. As there is considerable evaporation, more so in light than in the dark, dishes were weighed and the requisite amount of distilled water was added daily to the

exposed dish and after three days to the dish kept to the dark, so as to keep a uniform moisture content of 16% throughout the experiment. From time to time weighed portions of samples were taken out and analysed for ammonia nitrogen, nitrate nitrogen, total nitrogen as well as total carbon and percentage moisture. The determinations of the percentages of ammonia nitrogen and of nitrate nitrogen in the soils were carried out by following the method devised by Oslen (*Compt. rend, trav. lab, Carlsburg*, 1929, 17, No. 15). The percentages of total nitrogen were determined by Kjeldahl's method, whereas the percentages of total carbon by following the wet combustion method devised by Walkley (*J. Agric. Sci.*, 1935, 28, 598). The percentages of moisture in the soils were determined by keeping a small quantity of weighed soil in an electric oven at about 105° for a period of nearly 20 hours, and then finding out the loss in weight.

The results are shown in Tables I and II. Figures in the tables present the amount of nitrogen fixed in mg. per 100 g. of oven-dry soil.

TABLE I.

Exposed to sunlight daily for 8 hours (Temp. 30°–45°) (600 g. soil + 12g. canesugar.) Started on 10th February, 1939.

Nitrogen fixed per g. of carbon oxidised = 5.7 mg.

(Figures are in mg. per 100 g. oven-dry soil.)

Date of sampling.	NH ₃ -N.	NO ₃ -N.	Total N.	Total C.
Original soil.	1.1	0.9	48.0	365.0
13-3-39	1.1	0.9	48.0	1062.2
18-4-39	1.2	0.9	48.6	906.6
22-5-39	1.2	1.0	49.4	858.7
26-6-39	1.3	1.0	49.8	743.2
22-7-39	1.2	1.0	49.8	694.7

TABLE II.

Dark (Temp. 30° – 45°) (600 g. soil + 12g. cane sugar). Started on the 10th February, 1939.

Nitrogen fixed per g. of carbon oxidised = 3.3 mg.

(Figures are in mg. per 100 g. of oven-dry soil.)

Date of sampling.	NH ₃ -N.	NO ₃ -N.	Total N	Total C.
Original soil.	1.1	0.9	48.0	365.0
13-3-39	1.1	0.9	48.0	1113.1
18-4-39	1.1	0.9	48.2	973.2
22-5-39	1.2	1.0	48.8	905.3
26-6-39	1.1	1.0	48.3	827.7
22-7-39	1.2	0.9	49.2	756.6

The results in Tables I and II show that more carbon is oxidised from the soil treated with canesugar, when it is kept in the light than that when kept in the dark. It is also found that the content of nitrogen in the soils slightly increases both in the light and in the dark. In general, however, the percentages of total nitrogen in the samples exposed to light, are higher than those of the corresponding samples kept in the dark.

Thanks of the author are due to Dr. J. K. Chowdhury and to Dr. S. P. Raychaudhuri for their kind interest during the progress of this work. The author is grateful to the Government of Bengal, for the award of a Research Scholarship which has enabled him to carry out this work.

AGRICULTURAL CHEMISTRY SECTION,
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Received September 27, 1940.

A NEW REAGENT FOR THE ESTIMATION OF MERCURY AND COPPER.

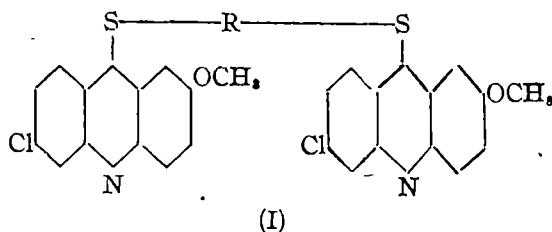
By S. J. DAS-GUPTA.

2-Chloro-7-methoxy-5-thiolacridine has been found² to be a good reagent for the estimation of mercuric and cupric salts.

It has been shown (Das-Gupta, *J. Indian Chem. Soc.*, 1940, 17, 244) that alcoholic solution of the sodium salt of 5-thiolacridine derivative reacts with neutral solutions of mercuric chloride and cupric sulphate forming insoluble mercurio-dithio- and cupro-dithioacridines (I, R = Hg or Cu) respectively. This reaction has been utilised for quantitative estimation of mercury and copper in their inorganic as well as organic compounds.

EXPERIMENTAL.

The reagent is to be prepared by dissolving 2-chloro-7-methoxy-5-thiol-



acridine (0.11 g.) in 95-100% alcohol (100 to 150 c.c.) mixed with 3.5 c.c. of *N*/10-alcoholic or aqueous caustic soda solution, and filtering the solution thus obtained. For estimating mercury, the compound is treated with strong or fuming nitric acid or other reagents to convert mercury into its soluble "-ic" form. The solution is then made just alkaline by adding caustic soda or sodium carbonate and then acidified by hydrochloric acid (excess should be avoided). In case of copper, the compound should be digested with little sulphuric acid so that a solution of copper sulphate is obtained.

A solution (about 10 c.c.) containing 10 to 20 mg. of mercury or 5 to 10 mg. of copper is best suitable for estimation. To the neutral solution, excess of the reagent is added and the mixture is to be stirred for some time and allowed to stand for several hours or preferably overnight. The precipitate, yellowish to red in the case of mercury, and pinkish brown in the case of copper, settles down and an orange to reddish supernatant

liquid indicates the excess of the reagent. 101 C.c. reagent is sufficient for 10 mg. of mercury and 5 mg. of copper. The precipitate is then filtered on a Gooch crucible and washed with 95% alcohol till the filtrate becomes almost colourless. The Gooch is dried in a steam oven and weighed. One gram of the precipitate is equivalent to 0.2676 g. of mercury and 0.09286 g. of copper. The copper derivative (I, R=Cu) contains 4 molecules of water of crystallisation. The results obtained are shown in the following table. Samples 1 and 2 were dissolved in strong nitric acid, 4 in fuming nitric acid, 5 and 6 in aqua regia, 7, 9 and 10 in strong sulphuric acid, while samples 3 and 8 were dissolved in water and directly treated with the reagent.

No.	Substance		Actual wt. taken.	Wt. of ppt.	Metal	
					found.	calc.
1	Mercury metallic	...	0.01128 g.	0.0421 g	99.88%	100%
2	Mercuric oxide	...	0.01505	0.0521	92.40	92.61
3	Mercuric chloride	...	0.01706	0.0471	73.89	73.85
4	Mercuric acetate	...	0.02082	0.0489	62.87	62.96
5	Mercurous chloride	...	0.01665	0.0530	85.19	84.96
6	Mercuric sulphide	...	0.01305	0.0420	86.14	86.24
7	Copper oxide	...	0.00759	0.0653	79.90	79.89
8	Copper sulphate (cryst.)	...	0.01542	0.0418	25.17	25.48
9	Copper acetate (cryst.)	...	0.01248	0.0428	31.84	31.86
10	Copper citrate	...	0.01464	0.0521	33.04	33.47

A freshly prepared solution of the purest sample of 2-chloro-7-methoxy-5-thiolacridine (m.p. 244-45°) should always be used. The acridine compound itself is sometimes precipitated due to the evaporation of alcohol or dilution during addition, but this is harmless, as it goes into solution by addition of more alcohol and is completely removed while washing the precipitate. If there is excess of inorganic salts in the solution to be estimated, these may be precipitated during dilution with alcohol, in that case the precipitate should be washed with water after removing the reagent. Acids and alkalis should be used to a minimum in preparing the solution.

The presence of the metals of groups I, II and III interferes with the estimation of copper and mercury. Those of IV and V have no effect. Notwithstanding this limitation, it is an accurate semi-micro method and may have varied applications.

The author desires to express his sincere gratitude to Dr. U. P. Basu for his kind encouragement during this investigation.

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Received September 19, 1940.

A NOTE ON THE ELECTROLYTIC ESTIMATION OF LEAD AS PEROXIDE.

BY DUSHYANT NARSINGASA SOLANKI AND T. V. SUBBARAO.

Rapid and accurate estimations of lead are required to be carried out very frequently in dye manufacture and other industries. Quite a large number of methods for the estimation of lead has been described in the literature. These may be classified as (i) gravimetric, (ii) volumetric, (iii) colorimetric, (iv) potentiometric, and (v) electrolytic methods.

It is known that in the electrolysis of aqueous lead salts lead separates more completely as peroxide at the anode than as metal at the cathode (Schucht, *Z. anal. Chem.*, 1883, **22**, 448; Luckow, *ibid.*, 1880, 1). Under the last mentioned condition, the cathodic deposit, being in the finely divided form tends to get oxidised even by atmospheric oxygen; its estimation as peroxide might be expected therefore to give better results. Another advantage of this procedure is that other metals *e.g.* copper can be deposited and therefore estimated simultaneously on the cathode. Despite a large amount of work in this field of lead deposition, considerable uncertainty exists on the precise nature of the anodic deposit; it may be (i) pure PbO_2 , or (ii) PbO_2 mixed with some other oxides of lead. Smith ("Electro-analysis", 1918, 6th Ed., p. 111) has worked out an arbitrary factor *viz.* 0.8643 to convert PbO_2 deposited anodically during the electrolysis, into lead; the chemical conversion factor, however, is 0.8662. The aim of the present investigation is to definitely establish whether there is any necessity of using any other factor than the chemical conversion factor.

Standard solutions of lead acetate and lead nitrate were prepared and measured volumes were taken for analysis. It was found by Joshi and Subbarao (*J. Indian Chem. Soc.*, 1938, **15**, 377) that stirring favours the formation of uniform deposits and allows the use of high current densities. Attempts to estimate lead by cathodic deposition on platinum electrode failed, since the deposit obtained from the acetate solution in presence of ammonium acetate and acetic acid could easily be washed off, or in any case, was not sufficiently adherent. Experiments were then made to estimate lead as peroxide on the anode. 25 C.c. of standard lead nitrate solution were taken in a beaker (Pb content = 0.1021 g.), 20 c.c. of conc. HNO_3 were then added and the solution made up to 100 c.c. with distilled water. A cylindrical platinum gauze was used as an anode and a rotating

platinum spiral (500-600 revolutions per minute) used as the cathode. The following were observed to be *optimum* conditions :

Voltage=3.0 to 3.1 volts ; current=3 amp. ; time = 30 minutes ; temperature=50-60° ; the wt. of PbO_2 =0.1178 g.; the wt. of Pb=0.1178 \times 0.8662=0.1021 g. .

Two more runs under the similar conditions gave the values for Pb as 0.1020 and 0.1019. The average value obtained was 0.1020, in agreement with the theoretical value, 0.1021. Similar agreements were obtained with lead acetate solutions in presence of 20% concentrated HNO_3 .

In all these experiments after the completion of electrolysis the platinum gauze anode with PbO_2 deposited on it, was carefully washed with distilled water, with rectified spirit and finally with ether and then dried at 190-200° for about half an hour, cooled and finally weighed.

The coincidence between the experimental and theoretical values using the ordinary chemical conversion factor 0.8662 shows that the introduction of the arbitrary factor 0.8643 is not justified. This further confirms MacInnes and Townsend's view (*Ind. Eng. Chem.*, 1922, **14**, 420) viz. lead peroxide is the only product of anodic oxidation and that no compound like PbO_2 , H_2O or any higher oxide is formed (*cf.* Smith, *loc. cit.*). The present method of estimation with the rotating electrode, is more rapid, simpler in manipulation and more accurate and can be used with advantage, for the analysis of lead salts in dye manufacture and other industries, in preference to potentiometric and other methods generally employed.

The authors are highly indebted to Dr. S. S. Joshi for suggesting the problem and valuable help.

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Received November 4, 1940.

RESIN PLASTICS.*

BY DR. H. K. SEN, D.Sc., D.I.C., F.N.I.

The choice of plastics as a subject for this address has been influenced by two main reasons : firstly, the ever-increasing share which plastic products are taking in the arts and industries generally during the last quarter of a century, and secondly, the absence of any plastics industry in India based on her own raw materials, natural or synthetic. Whilst the production of synthetic plastic materials is dependent on an all-round industrial development, the existence of the natural resin in shellac in the country raises the question whether this unique raw product could not be the basis of a commercially feasible plastic industry i.e., in reasonable competition with synthetics. It would appear from statistical considerations that the demand for shellac has gone on continually increasing, and in fact, from an export figure of 308,937 cwt. in 1920-21, it stands at 760,399 cwt. in 1939-40 in spite of the tremendous output of various synthetic resins in the countries importing shellac. This alone is proof positive of the superiority of this natural product over many of the synthetics, at least in certain industrial uses. About 300,000 maunds (11,000 tons) of shellac are consumed by the gramophone record making industry, which the synthetic resin has scarcely been able to penetrate into. The largest application of synthetics is in the moulding of household articles, specially, electro-technical, and how far shellac as such or modified can be substituted would be discussed later. When an industry is faced with the disposal and utilisation of its by-products, a sort of inevitable competition between such products and similar natural or agricultural products makes its appearance, and the fate of the natural product is determined by its performance efficiency and price as compared with its synthetic rival. Vested interest actuates the producers of both the synthetic and the natural product, and the consumer, who has ultimately to face the music, would naturally welcome the presence of both commodities in the market for his choice. Improvements by research for ultimate processing of both classes of materials is, therefore, an important feature in the economic development of industries dependent on them. There is, however, another aspect of the problem—the combination of the natural with the synthetic product to suit local conditions or

* Address delivered at the Annual General Meeting of the Indian Chemical Society held on 6th of January, 1941 at Benares,

secure better performance, which has not attracted the attention it deserves. Whilst a review of the synthetic resin industry with special reference to its development in India will be at first attempted, later, specific cases of quasi-synthetic plastic materials will be discussed and their value in national economy clearly indicated. It is hoped that the attention of the State will be directed to an enquiry whether a plastics industry based on India's natural products cannot be developed, and, if so, what steps it should take to bring such an industry into being.

Plastic resins may be classified into two groups—thermoplastic and thermo-hardening.

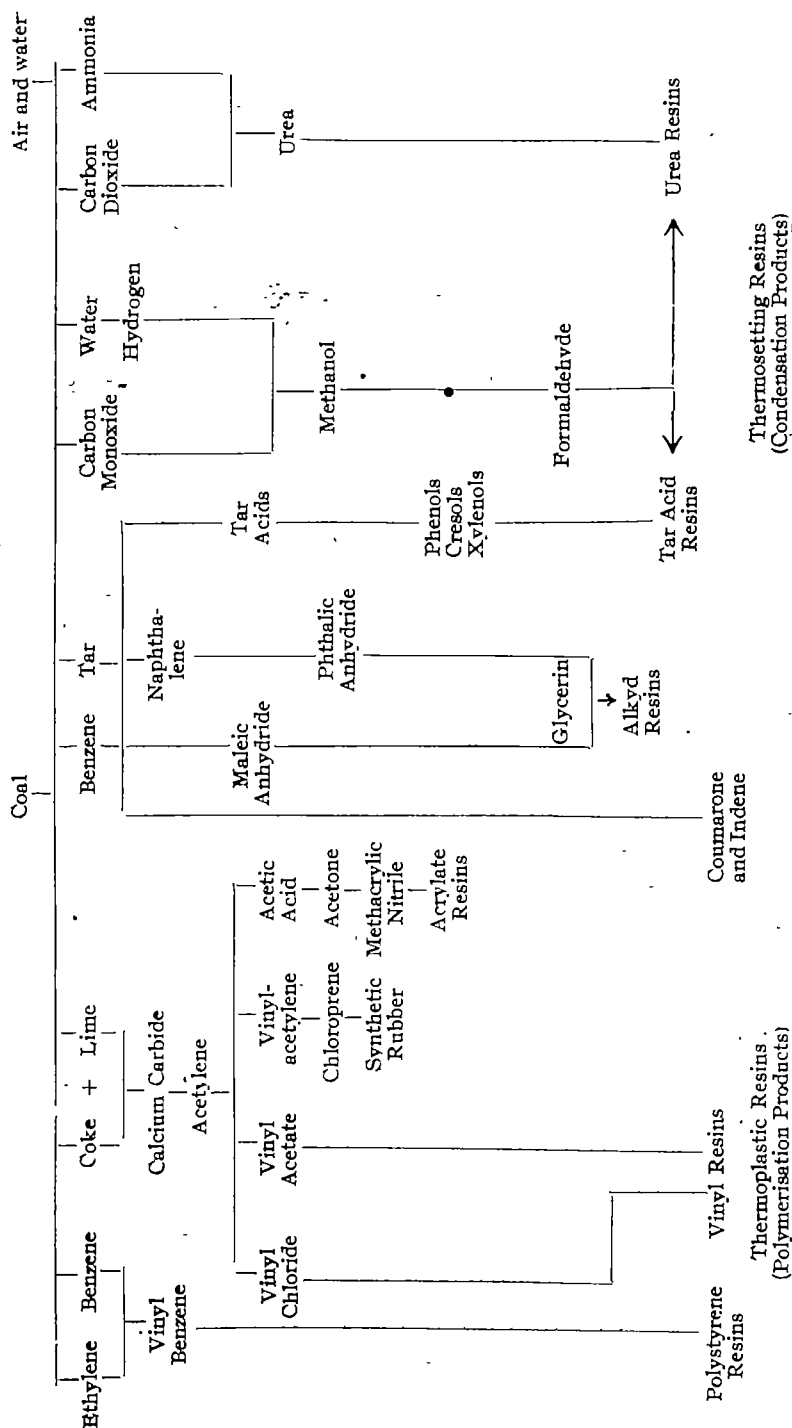
A. Thermoplastic resins:—Shellac, glycol polybasic acid resins, vinyl resins, polystyrene, polyindene, novolacks, protein resins, etc.

B. Thermo-hardening resins:—Phenol-aldehyde resins, urea-aldehyde resins, heat convertible alkyds, etc.

A consideration of the composition of synthetic resins would reveal that a few raw materials, which are by-products of some principal industries, are chemically and physically treated to produce high molecular or polymeric compounds with adequate plasticity which either remains intact during moulding or is changed thereby. The chart on p. 49 illustrates the sources of raw materials.

The availability of such starting materials is the condition precedent for the development of a synthetic resin plastic industry in this country. Looking at the chart it cannot be said that raw materials for synthetic resins are as yet available at such prices and in requisite quantities that can warrant the laying down of the foundation of this industry. There appears, therefore, to be a decided advantage, for the time being at any rate, in favour of natural or quasi-natural plastics. Taking the case of bakelite, the most important of the synthetic resins, the two essential materials, phenol and formaldehyde are as yet not available, particularly the latter, the manufacture of which is still only a project. As to phenol, no doubt a quantity of it could be had as a by-product of the coking industry, but its price is far too high in the present state of the tar-distillation industry to allow of its being used in plastics production. As for formaldehyde, there is at present methyl alcohol available at the Mysore Iron Works, Bhadravati, at a cost of Rs. 3/8, per gallon, but synthetic methanol costs only 11d. This is by

THE DERIVATION OF CERTAIN SYNTHETIC RESINS



From U. S. Tariff Commission Report No. 131 "Synthetic Resins" with Coumarone and Indene added.

way of the economics of bakelite manufacture in India.* Considering however, that the availability of these two raw materials, phenol and formaldehyde, is probable in the near future, the investigation of problems relating to the technical manufacture of bakelite should engage the attention of research chemists. The theory of bakelite formation is tolerably well-understood by now, but investigation on the plastic nature to effect further improvement is far from complete. Then again, a whole range of experiments with different phenols and bi-phenols might lead to still superior products, whilst the problem of fillers, especially, wood flour from Indian wood, has not yet been touched.

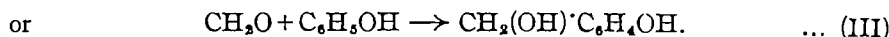
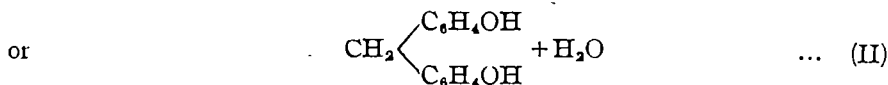
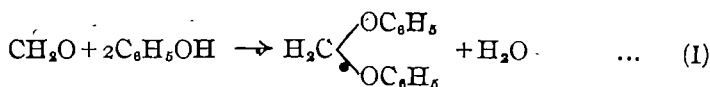
The next important synthetic resin is that derived from the condensation of urea with formaldehyde. Here again, the manufacture of urea by the cheapest possible process has to be brought into existence in this country before this type of resin could be manufactured economically. Many are the methods suggested for the production of this important chemical, but its synthesis from carbon dioxide and ammonia and production from calcium cyanamide are the two practicable processes so far developed for its manufacture. These methods have been tested on more than a laboratory scale at the Indian Lac Research Institute, as this chemical and a few allied ones (*vide infra*) have been found to be excellent accelerators in the manufacture of moulding powders from shellac and modified shellac. A semi-large scale plant for and method of operation of each of the processes are described in 'Practical Applications of Recent Lac Research' published by the Indian Lac Research Institute.

PHENOL-FORMALDEHYDE.

As early as 1872, Baeyer studied the reaction products of benzaldehyde with pyrogallol acid and resorcinol, acetaldehyde or chloral with resorcinol, methylene acetate with phenol, etc. He established the fact that aldehydes and phenols, under suitable conditions, yield resinous products. Smith in 1900 and many others before him had noticed the reaction, and in fact, Trillat in 1896 had described the condensation of phenol and aldehydes in the presence of mineral acids and exhibited several artificial resins in the Paris Exhibition of 1900. The merit of Baekeland lay, however, in the discovery that under pressure and heat such resins were converted into

* Several cheap sources of formaldehyde are indicated in recent patent literature. These are ethylene, methane, coal-gas, etc. In the absence of cheap synthetic methyl alcohol, experiments on the conversion of low-temperature carbonisation gas and ethyl alcohol into formaldehyde are being attempted at the Indian Lac Research Institute with promising results. The catalytic oxidation is conducted under ordinary atmospheric pressure, and as such there are less plant constructional difficulties.

insoluble and infusible substances. The theoretical basis of every such reaction is well understood until the stage at which a thick syrupy or pasty mass is produced. Opinions differ as to the interpretation of the further course of resinification by polymerisation and condensation. Several hypotheses based on experimental evidence, analogies and theoretical considerations have been advanced. Phenol and formaldehyde react resulting in either a diphenyl ether (I) and a methylene diphenol (II), by condensation, in an acid medium, or an aldol formation (III), by addition, in an alkaline medium :—



The formation of the diphenyl ether (m.p. 18°), methylene diphenol (m.p. 160.2°) and hydroxybenzyl alcohol (m.p. 87°) has been demonstrated. By the application of heat, the alkali-catalysed products polymerise and Baekland considers that a ring compound is formed, whereas Herzog and Kreidl believe that the molecule exists as a lattice structure. The acid-catalysed resins are permanently soluble and fusible and are not much in use.

Equimolecular proportions of phenol and formaldehyde (94 g. of phenol + 75 g. of formalin) with 1% by weight of concentrated ammonia are digested at 80°–90° and cooled, when the mass separates into an aqueous upper layer and a pale straw-coloured liquid. The water and traces of uncombined phenol are removed by vacuum distillation at 65°–70° and the resin is discharged into shallow trays and cooled quickly. An important variation in this process is to condense phenol with part of the formaldehyde in the presence of alkali or acid and after dehydration, to add hexamethylenetetramine. Other aldehydes like furfural, and phenols like cresols and resorcinol, when cheap and abundant, are used for making similar resins.

It may be mentioned in this connection that almost all the synthetic resins are formed by condensation reactions in which generally water is eliminated and sometimes halogen hydrides, hydrogen sulphide, ammonia or hydrogen are liberated. If the resulting products contain residual unsaturation points or double bonds, they are non-hardening. Resins, as mentioned above, may be divided into two types : permanently fusible resins or thermoplastic, and those which are polymerised to an infusible state by heat and pressure or thermo-hardening resins. With this criterion of resin formation, it can be imagined what an endless variety of resins is

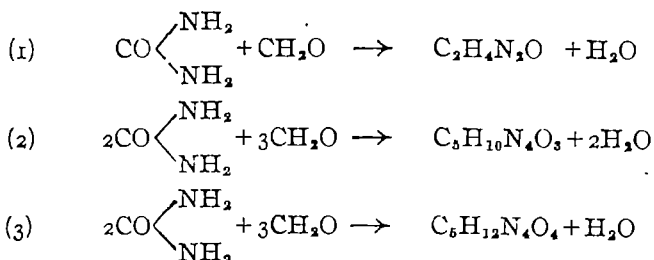
possible and chemists all over the world have vigorously pursued this line of investigation for the last 28 years i.e. ever since Dr. Baekeland established the commercial success of phenolic synthetic plastics. Every variation of the reactants, catalysts, and various modifying agents are being examined. But among all the known synthetic resins for plastics, although a few might be preferred to phenolics for special applications, none has approached the great commercial success attained by the latter. Phenol-formaldehyde resins are used for many other industries besides plastics in which latter field they are either used as castings in the shape of rods, tubes or imitation jewellery or as composite mouldings when mixed with fillers, dyes or pigment. The moulded articles are used in electrical insulations, household appliances, scientific apparatus, machinery, etc.

UREA-FORMALDEHYDE RESINS.

Although phenol-formaldehyde resins enjoyed a large measure of popularity within the first decade of their commercial development, the aesthetic tastes of the public demanded moulded materials in lighter shades of colour than the black, brown and dark green of the phenolics. Urea-formaldehyde resin moulded articles, otherwise called amino-plastics, were the answer to this need. Amino-plastics are only second to phenolic plastics and moulded articles in all pastel shades from glass-like transparency through varying degrees of translucency to opacity are available.

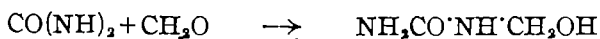
It was known as early as 1884 that the reaction between urea and formaldehyde results in resin-like materials, but it was in 1896 that the definite nature of the reaction under *neutral*, *acidic* and *alkaline* conditions was investigated and understood. The commercial application of such resins for moulded articles started as recently as 1921, and Poliak established the conditions necessary for producing mouldable substances between 1920 and 1927.

The products formed by the reaction of urea with formaldehyde vary according to the proportion of the two and the p_H of the medium. Their composition and properties are also different. In acid solution, the following reactions take place :—

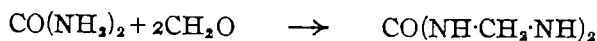


The end-products occur as polymers, although their chemical compositions are as indicated by their monomeric formulae. $(C_2H_4N_2O)_x$ is an amorphous powder, slightly soluble in water and splits up again into the original constituents by the action of mineral acids. $(C_6H_{10}N_4O_3)_x$ is obtained as a granular precipitate when the amount of formaldehyde used is 1.5 to 2 molecules per molecule of urea. Higher proportions of formaldehyde result in $(C_6H_{12}N_4O_4)_x$ in smaller yields.

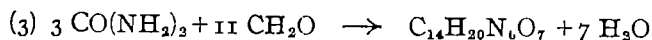
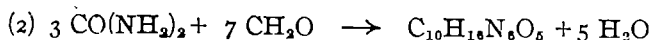
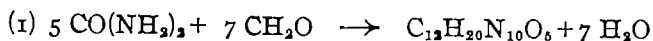
When formaldehyde is added to a solution of urea and barium hydroxide in water at 0° , (*i.e.* in alkaline solution) monomethylol urea is formed.



The product is easily soluble in water and in methyl alcohol but insoluble in ether. It crystallises from alcohol in prisms with a melting point of 111° . On the other hand, when urea is added to barium hydroxide in formaldehyde solution at 25° , dimethylol urea is obtained, which is soluble in warm ethyl or methyl alcohol. It melts at 126° to a liquid which again solidifies at 138° with the liberation of water and formaldehyde, which, on heating further, decomposes without melting at 260° .



In neutral solutions, the following three reactions have been found to take place according as one, two, or more molecular proportions of formaldehyde are reacted with urea.



Urea-formaldehyde resins find applications in the field of adhesives, glass substitutes and moulded wares. According to the nature of application, different methods of producing the resins are adopted, and numerous patents have been taken out claiming diverse properties. A typical method of producing glass-like masses is as follows:—

One molecule of urea and 2 molecules of formaldehyde are heated under reflux in the presence of hexamethylenetetramine until a clear, homogeneous liquid is produced. At this stage, a small quantity of sodium acetate is added to the liquid to prevent quick gelation and then most of the water is removed by vacuum distillation. Urea is again added to neutralise the acid reaction of the product and also to combine with the unreacted formaldehyde. Water is then distilled off and the product is hardened

at 60-100° in moulds. Addition of sodium chloride during the final distillation helps to yield a clear glass-like product with a specific gravity of 1.44 and a refractive index of 1.5-1.9, and a hardness nearly equal to that of copper.

For the manufacture of moulded articles, the resin after the water has been distilled off and when it is still soft, is mixed with 30-40% of its weight of paper pulp or pure cellulose fibre and dried at 50° in a vacuum oven. The dried mass is finely ground, mixed with a small proportion of salicylic acid and glycerine or resorcinol and used as a moulding powder. Salicylic acid helps to polymerise the resin thoroughly during the process of moulding and glycerine or resorcinol prevents sticking of the moulded articles to the mould surface.

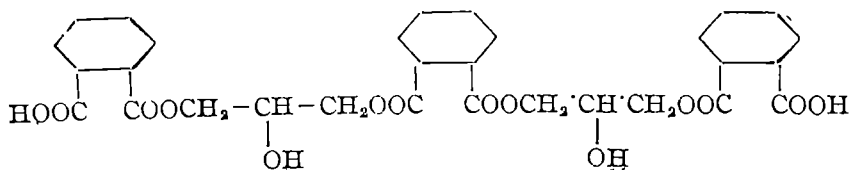
In the above process, if thiourea is substituted for urea, much stronger products result but higher temperatures are necessary both for the formation of the resin and for the moulding operation.

Recently, very useful resins have been produced by condensing melamine with formaldehyde and other naturally occurring substances containing aldehyde groups. Such resins are water-clear, transparent, tough and resistant to water.

ALKYD RESINS.

Under this class come the resins formed by the condensation of glycerol and various polybasic acids or their anhydrides, principally phthalic anhydride. India is now in a position to meet her requirements of glycerol and she can also produce phthalic acid by the vapour phase oxidation of naphthalene derived from her gas works and coke-oven tars. No serious difficulties are anticipated in the manufacture of this resin or its modifications which have proved of more value as varnishes, lacquers and adhesives than as plastics.

The chemical reaction is simple and as the type of polybasic acids can be varied, various grades of alkyd resins can be produced to suit special requirements. Kienle and his co-workers are of the opinion that in the esterification of glycerol with dicarboxylic acids, two molecules of the former give rise to an intermediate compound as follows :



This compound is considered to be the monomer of the polymerisation product which can be formed by the interaction of the remaining carboxyl groups with the β -hydroxy groups of the intermediate compound. To illustrate, 31 parts of glycerine and 74 parts of phthalic anhydride are heated together at 180°-200° until a drop of the product, when cooled, has a melting point of 90°. From local considerations, it would appear that a pound of glyptal may be produced at as low as 12 as. which is considerably higher than the price of most natural resins. Alkyd resins possess good adhesive, electrical, mechanical and thermal properties but their thermosetting is very slow. When polymerised, the resin is resistant to water and chemicals. A long range of products may be obtained by modifications effected by reacting with other organic acids, drying and non-drying oils, natural resins, etc. Recently, at the Indian Lac Research Institute, glycerol has been replaced by aleuritic acid, (1-hydroxy-7:8-dihydroxypalmitic acid) derived from the hydrolysis of shellac, and a solid resin functioning as a good plasticiser has been isolated. The use of lactic acid as a substitute for glycerol in the formation of alkyd resins has also been reported by Stearn, Makower and Groggins (*Ind. Eng. Chem.* 1940, **32**, 1335), and the cheap production of the acid by fermentation would constitute a first step towards commercialising this interesting resin.

ETHENOID RESINS.

(i) *Acrylic acid Resins.* Of late, glass-clear resins, prepared from polymerised acrylic acid or its esters, have largely been used for automobile parts, air-craft industry, watch crystals, prisms and lenses. The starting materials for the manufacture of these resins are ethyl alcohol and carbon dioxide which may be available at a cheap cost in this country. With the large quantity of molasses as a by-product of the sugar industry, both ethyl alcohol and carbon dioxide could be obtained in abundant quantities. A mixture of ethyl alcohol and carbon dioxide is passed over a dehydrating catalyst to first convert alcohol into ethylene. This mixture is then led into a chamber maintained at 200-300° and reacted in presence of a catalyst (*e.g.* sulphur dioxide, sodium acid phosphate) to form acrylic acid $\text{CH}_2=\text{CH}\cdot\text{COOH}$. Polymerised acrylic acid is itself resinous, but generally methyl or ethyl esters are used. Polymerised acrylic acid and its esters are glass-like thermoplastic resins which are sold in the form of sheets or powder and are eminently fitted for moulding curved or intricate glass-clear articles. The resin is sold under the name

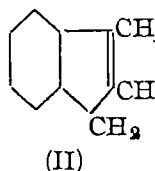
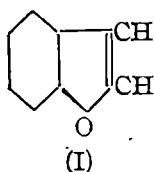
of Leucon, Perspex or Diakon in England and as Plexiglass, Plexigum and Acryloid in Germany and America.

(ii) *Vinyl and Styrol Resins.* When acetylene is conducted rapidly through glacial acetic acid in the presence of mercuric sulphate at 70° , vinylacetic acid ($\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{COOH}$) is obtained which is then polymerised into straight chain polyvinyl acetate by heat. Polyvinyl acetate polymerises to hard infusible masses on heating at 100° . Polymers of vinyl halides are prepared from acetylene and these are less soluble and stable than the esters. It is only the co-polymer of the halide and the ester that finds a large application in industries for the manufacture of gramophone records, dentures, brush handles, tumblers, glass substitutes, etc.

Styrene or vinylbenzene ($\text{CH}_2=\text{CH}\cdot\text{C}_6\text{H}_5$) is a colourless liquid, (b.p. 145°), prepared from ethylbenzene by pyrogenic dehydrogenation or by chlorinating and removing hydrochloric acid. It is polymerised into several grades of resins by carrying out the operation at low temperatures (100°) or high temperatures (180°) or in the presence of catalysts like oxygen and peroxides, acids, halides, alkalis. The resins produced are all glass-clear and have melting points ranging from 100° to 180° . Polystyrene resins are perfectly thermoplastic and are ideal for electrical insulations, and for injection moulding.

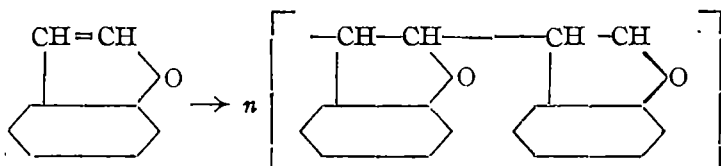
COUMARONE AND INDENE RESINS.

Coumarone resins are prepared from coal-tar fractions boiling at 150° - 200° . On redistillation, a fraction is obtained containing about 30% of polymerisable compounds, these compounds consisting chiefly of coumarone (I), the isomeric methyl coumarones, indene (II) and possibly isomeric methylindenes. Sulphuric acid is used as the polymerising



catalyst, an appropriate amount of which is run into the liquid with stirring. The reaction temperature favours the production of dark coloured resins. When viscosity determination shows that polymerisation has reached its maximum, the liquor is neutralised, washed, tar decanted off, and the

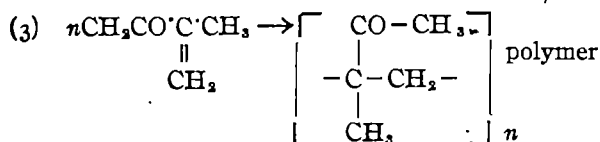
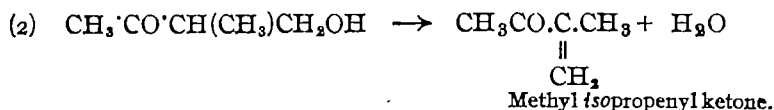
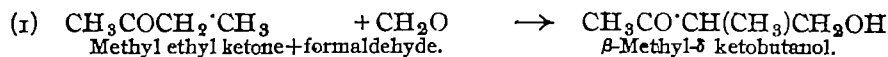
residual liquor distilled in vacuum to give yellowish, permanently fusible resins. Polymerisation is believed to be of the following nature :—



Coumarone resins are yellowish in colour and not particularly light-stable. They are oil-soluble and used largely for certain types of alkali-resistant coating compositions, printing inks and in rubber compounding. These resins have found only a limited application in the plastics industry because, although they are cheap, resistant to moisture, and excellent as electrical insulating materials, they are too brittle and possess a low tensile strength.

KETONE RESINS.

The process for the production of ketone resins consists in condensing acetone with formaldehyde in the presence of a mild alkaline catalyst to give a mono methylol derivative, a keto-alcohol, which is treated with one of the common dehydrating agents to give a methylene derivative—an unsaturated ketone—which can be polymerised by heat and light, to give a thermoplastic resin. It was found, however, that by using acetone, the two preliminary stages were apt to get out of control. Hence the homologue, methylethyl ketone is now used in preference to acetone, as the reactions are more readily controlled. The reactions involved with methyl ethyl ketone are :



The resin is tough, colourless, transparent, machinable, thermoplastic and acetone-soluble.

CASEIN PLASTICS.

Casein, obtained by the treatment of skimmed milk with rennet, is the raw material for casein plastics manufacture. This casein, conforming to certain standards, particularly with regard to ash, fat and sugar content, is left with about 30% of its weight of water in the cold, until the casein particles are completely hydrated to casein gel. Colouring matters are generally added during this mixing stage. The gel is homogenised and moulded to a composite mass by passing through an extruding machine which consists essentially of a heated barrel in which operates an Archimedean screw which forces the material through screens and then through a heated nozzle at the end of the barrel. By this means rods of considerable length might be extruded, the size and shape of the rod being controlled by the nozzle. The rods are then soaked in dilute formaldehyde solution (about 5% CH_2O) until the formaldehyde has penetrated right through the material, the time of soaking obviously depending upon the thickness of the rods. This formalising process hardens the casein material rendering it tougher and less susceptible to moisture. After formalising, the rods are dried, straightened, tapered to constant diameter and are mop polished or given a high gloss by treatment with sodium hypochlorite solution. The rods can be converted into sheet forms by hot pressing before hardening with formaldehyde. By far the largest use of casein plastics is for buttons and buckles for womens' clothes. Other uses of casein material are for knitting pins, combs, etc.

The total world production of casein is estimated at 70,000 tons a year, out of which about 10,000 tons may be used in the field of plastics.

The general drawback met with in casein plastics is the time required for formalising casein in order to make it water-resistant. The presence of certain high paraffinic acids has a tendency to impart water-proofness to casein plastics, but as a rule, the water absorption is still much too high. Compounding ammoniacal shellac and casein in the presence of potassium stearate and precipitating them with alum, a resin is obtained which can be moulded between 110-120° with good gloss and satisfactory water-resistance.

NITROCELLULOSE AND CELLULOSE ACETATE.

The raw material for the production of nitrocellulose for plastics is generally purified cotton linters. This material consists of cellulose

$(C_6H_{10}O_5)_n$, with three hydroxyl groups per $C_6H_{10}O_5$ or anhydroglucose unit. Nitrocellulose is a misnomer since the products obtained from cellulose and nitric acid are esters, the correct term being cellulose nitrate. For each anhydroglucose unit there are three nitrate esters possible. Cellulose nitrate containing about 11 % of nitrogen approximating to dinitrate and soluble in alcohol is the grade preferred for plastics manufacture.

The nitration of cellulose is carried out below 35° by treatment with a nitration mixture consisting of 80% solution of sulphuric and nitric acids in 3:1 proportion. The nitration is completed in 20 minutes and the resulting product contains 10.5 to 11.1% nitrogen. The material is precipitated in water. The nitrocellulose is then centrifuged for the removal of water, final traces of which are removed not by drying but by leaching out with methylated spirits. The damp mass is mixed and kneaded with 30% of camphor, dyed or pigmented, and then rolled into sheets. They are then placed in seasoning rooms under controlled conditions of humidity and temperature to remove alcohol and moisture. Warping can be corrected by pressing the blocks between polished steel platens; 80% of pyroxylin plastics produced are in the form of sheets, about 15% is marketed as rods and 5% as tubes. It is estimated that there are over 25,000 uses for celluloid. It can be produced in an infinite variety of colours and patterns. Celluloid is among the toughest and strongest plastics known and was first prepared in 1868 by John W. Hyatt.

CELLULOSE ACETATE.

For a long time there had been a search by chemists for non-inflammable celluloid. Schutzenberger first acetylated cellulose in 1861. Cellulose acetate, freshly prepared, is unstable and decomposes rapidly in the presence of water. In 1905, G. W. Miles discovered that by ripening the ester at 30° a definite improvement in physical properties takes place.

Cotton linters are added to a mixture of acetic acid, acetic anhydride and sulphuric acid and the temperature is maintained below 20° . In 2 to 6 hours, a thick syrup will result, from which the acetate is precipitated by dilution with water, benzene or petroleum ether. This is maintained at 30° for 5 or 6 days and then filtered and dried. Butyl lactate, butyl phthalate, phenol phthalate and phenol lactate are some of the plasticisers used; 10-30% plasticiser are added and further processing is the same as for celluloid.

Ethyl cellulose and benzylcellulose, prepared by treating alkali cellulose with ethyl or benzyl chloride, are recent products that are finding increasing applications.

An important use of celluloid and cellulose acetate is in the manufacture of photographic and cinematographic films.

LIGNIN.

The chief constituents of wood are cellulose and lignin, 20-30% of lignin usually being present. The cellulose unit, since it has not a benzenoid structure, may be considered as aliphatic, whereas lignin is definitely aromatic in structure. Lignin is a compound of carbon, hydrogen and oxygen, but is not a carbohydrate. As would be expected, therefore, lignin has properties very different from cellulose. The lignin unit has been found to contain reactive groups which are capable of resinification with either phenols or aldehydes when heated, preferably in the presence of a catalyst.

Various methods have been proposed for the production of resinous products from lignin. Wood flour or saw dust is commonly used as the raw material, the lignin complex being resinified, the cellulosic component being substantially unchanged and remaining as filler. For example, wood flour and about a quarter of its weight of phenol plus a little hydrochloric acid or ammonia may be heated together, dried and pulverised to give a thermosetting composition which would contain about 50 % of cellulosic material as filler. The product obtained is dark coloured and can be hot pressed. Similar products are claimed to be produced when furfural is used in place of phenol. The bulk of the commercial development of the manufacture of lignin moulding compositions is being carried out in U.S.A.

RUBBER PLASTICS.

Plastic materials for electrical insulation may be obtained from rubber and formaldehyde, or rubber, formaldehyde and phenol. Such bodies have certain properties of both hard rubber and phenol resin. For the preparation of the moulding material, crepe rubber or latex can be used. A typical composition is prepared as follows:—15 kg. of pale crepe rubber are dissolved in 300 kg. of carbon tetrachloride, 25 kg. of sulphuric acid (sp. gr. 1.14) being stirred in to serve as a condensing agent. 40 Kg. of 40% formaldehyde solution are added, and the mixture is refluxed for 2-3 hours at 100°. The resulting greyish white product, containing free acid, formaldehyde and carbon tetrachloride, is treated with 100 kg. of water and carbon tetrachloride distilled off, about 90% being recovered. The mass is washed with running water until free from acid, dried and milled in a cold mill.

Then it is heated at 95° until dry. The brownish black powder, which is obtained finally, can be moulded at 140° - 160° under a pressure of 3000-4000 pounds per sq. inch. It has a specific gravity of 1.95 at 11° , softens at 130° , has a transverse tensile strength of about 400 pounds per square inch and is almost insoluble in all acids, bases, and organic solvents. The moulded articles take a high polish and may be machined, turned, sawed or drilled.

FILLERS.

The various resins described above are not generally used alone for moulding, but they are incorporated with some more or less inert materials, called fillers, the resin functioning as a cementing or binding material. The proper selection and preparation of fillers have pronounced influence on the properties, cost and performance of the finished articles. In general, the addition of fillers to synthetic and natural resins reinforces them and modifies their relatively brittle nature and heat resistance. A satisfactory filler must be cheap and plentiful. Its constancy in composition, *i.e.* freedom from adulterants, impurities, dirt, conducting particles, and excessive moisture, must be invariably secured, and it must be inert and capable of being 'taken up' by the resin with which it is used. It must not also evolve gases under moulding conditions or subsequently.

Mouldings intended to resist high temperatures must be filled with inorganic materials, such as asbestos, mica, chinaclay, magnesia, etc. Mouldings intended for operation at moderate temperatures are usually filled with wood flour. This is the most useful filler and it is cheap and plentiful. The mechanical strength of mouldings designed to stand moderate temperatures is increased by the introduction of a proportion of vegetable fibres such as cotton flock.

The fillers commonly used in moulding compositions may be classified under two divisions: (1) Vegetable—Wood, cotton, hemp, flax, jute; and (2) Mineral—Asbestos, magnesia, chinaclay, mica, slate dust, marble, gypsum; lithopone, titanium oxide, zinc oxide etc. *Wood flour* is one of the most widely used fillers. The most suitable woods are varieties of pine and spruce, not too rich in rosin or oil. In the manufacture of wood flour, the wood fibres are disintegrated either mechanically or chemically, care being taken not to destroy the smallest fibre units by excessive disintegration. As a rule, therefore, wood is ground, or treated under pressure and heat with alkali to obtain the requisite fineness. Generally, 80-100 mesh powder would suffice to give the necessary strength

to the moulded articles. A highly fluffy powder is unsuitable as the bulk of the moulding powder must be low in order to obviate the use of larger moulds which are difficult to make and are also costly.

PREPARATION OF MOULDING POWDERS.

The most widely used procedure for mixing the thermoplastic and particularly the thermosetting moulding composition is the 'dry method' which eliminates the need for solvents and their subsequent removal and recovery. When large amounts of liquid or plastic binders of low softening point are used, the dry process gives a uniform product. This method consists essentially in pulverising the resinous binder and grinding this with other ingredients, lubricant, flux, hardening agent and dyes. The work may be done in a hammer mill or ball mill. The fibrous fillers such as wood flour, cotton flock, asbestos etc. are then added and the blending continued until a uniform mixture is obtained. The light, fluffy powder, prepared in this manner, may be given additional treatment by passing between heated steel cylinders revolving towards each other at slightly different speeds. These are so arranged that the distance between the rolls may be varied during operation at the will of the operator to process the material properly and obtain a sheet of desired thickness. The sheeted material or the blankets are removed from the rollers, cooled and powdered in disintegrators and stored. The loose powders are tableted prior to moulding to reduce bulk and avoid entrapped air, and sometimes preheated to save time in the press or to remove traces of moisture.

SHELLAC.

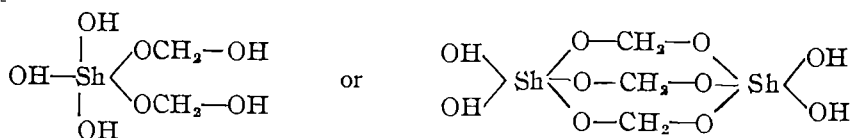
Shellac is one of the oldest plastics known to civilisation. The fusibility and accurate seal reproduction of sealing waxes were known in Europe during the middle ages. A shellac-moulded casket with elaborate engravings was produced in Birmingham in 1876. As an improvement over rubber mouldings as regards surface finish and speed of output, shellac mouldings came to be adopted for moulded electrical parts. The real impetus for shellac plastics came with the manufacture of gramophone records about the year 1900, in which field it is still supreme, despite hundreds of synthetic resins that have tried to replace it. The present-day synthetic resin plastics industry owes its existence indirectly to shellac, because it was the high price of shellac at Rs. 200 a maund in 1905 that led to the search for synthetic shellac, failure to attain which incidentally resulted in the discovery of commercially practicable synthetic resins. As already stated, the success

attained by Bakelite in 1912 has led chemists all over the world to make fresh discoveries in this ever-widening field of new resins.

India has practically a monopoly of lac production being responsible for about 90%, the rest being grown in Burma, Thailand and Indo-China. The average of the last 10 years' production is nearly 30,000 tons per annum, out of which at a modest estimate, about 10,000 tons are used in the plastics industry every year. The major part of the consumption in the plastics field goes into the production of about 200 million pieces of gramophone records annually, and a small fraction is used in the manufacture of laminated paper and mica articles, grinding wheels, and small dials, knobs and discs for electrical and radio industries.

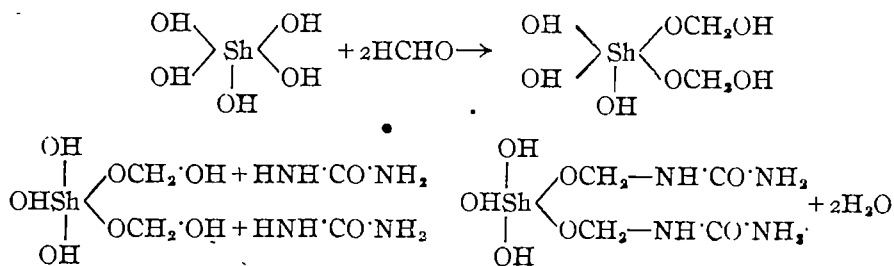
If shellac compositions are to be more widely used for plastic moulding, they should be capable of being produced at a faster rate than by the hot and cold process and should be much more heat and water resistant than the gramophone record compositions. Recent investigations at the Indian Lac Research Institute have shown that shellac modified by formaldehyde, urea (British Plastics, April, 1939), melamine (*Indian Lac Res. Inst. Res. Note No. 22*), etc. could be worked on the hot moulding technique and shellac modified with formaldehyde and guanidine carbonate filled with jute waste could be injection moulded. The heat resistance of the modified shellac moulded articles is about 90°, and is, therefore, suitable for most purposes. By gradual after-baking, the resistance could, however, be raised to 120° and more.

The theory underlying the modification of shellac by formaldehyde is as yet obscure, but there is sufficient evidence from experimental data that the interaction of shellac with formaldehyde gives rise to a shellac formal:



On heating shellac with formalin for 1-1½ hours, subsequent washing of the product with several changes of hot water, a formal derivative containing 4-6% formaldehyde is obtained which liberates formaldehyde on keeping only slowly. This formal is more plastic than that of shellac itself, and has a softening point of 68°, about 10° lower than shellac. The chief distinguishing characteristic of the formal is its slower polymerisability *i.e.*, longer life under heat. With urea, sufficient heat resistance is developed without giving rise to brittleness even at higher temperatures and longer 'curing time.' The interaction

of urea with the shellac-formal does not, however, completely convert it into a perfectly thermo-hardening material, but urea confers to the formal sufficient thermosetting characteristics to impart to filler-filled moulding powders adequate toughness to enable ejection of moulded articles at temperatures between 140° and 150° without having to take recourse to cooling. The mechanism of the action of urea on the formal may be expressed as below :



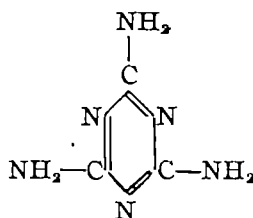
This would show that resin formation under these conditions is a quasi-synthetic process, and whilst the totality of the reaction between shellac, formaldehyde and urea produces eventually a resin lying in the borderland of thermosetting and thermoplastic ones, its superior electrical properties, good impact resistance of moulded articles (as high as 8 rcm/kg/cm^2), and cheapness would speak for the feasibility of this resin being commercially used in the plastics industry. The essence of the reaction with urea is indeed to build up high molecular polymers with the shellac formal, and probably the inability to build still higher polymers is the reason for inferior thermo-hardening properties of this quasi-synthetic resin. Further researches are expected to overcome this difficulty, but the borderland property of the resin enables rejected moulded articles to be recrushed and reused for further moulding. This by itself is of no small advantage, as synthetic thermo-hardening resins do not lend themselves to such operations.

The introduction of a formal grouping in shellac has a most important bearing on the chemical reactivity of the rather inert shellac molecule. In fact, this formal formation has made it possible to bring about condensation of shellac with phenols, the resulting resin having certain good characteristics both for varnishing and plastic moulding purposes. The interaction of 5-10% of phenol with shellac-formal improves the flow of the final resin, but it is still not thermosetting in the sense that bakelite is. The mechanism of the reaction of phenol with shellac-formal is under investigation, but that the condensation is

of a type different from that of bakelite formation is concluded from the fact that the action of urea is necessary for the formation of a suitable resin. The properties of the mechanical mixtures of shellac and bakelite in varying proportions were studied by Ranganathan and Murty (*private communication*.) These are different from the resin now produced by condensation of phenol with shellac formal. The phenomenon of co-polymerisation might be responsible for the improved properties noticed in the latter case.

Mention must be made here of the effect of melamine on the polymerisation of shellac-formals. This chemical, which is assuming importance of late, can substitute urea, and the function of the amino group in the resin formation becomes clearer, as quantities of urea and melamine used to produce the same effect are proportional to the amino groups present in them.

Resins have been prepared at the Indian Lac Research Institute with shellac-formal and melamine,



which are transparent and more thermo-hardening than those with urea and shellac-formals, but they have the disadvantage as yet of being somewhat brittle. Excellent baking varnishes are, however, produced from the shellac-formal-melamine resin with the addition of small quantities of plasticisers. A typical modified shellac moulding powder is prepared as follows :-

The proportions of the different materials employed are :

*Lac	50 lb.
Formalin (35-40%)	25 "
Urea	7'5 "
Calcium stearate	1'25 "
Pigment (brown, black or red)	2'5 "
Wood flour	50'0 "
Rectified spirit	20 gallons

The above materials are digested in a steam-jacketed still, by using steam at 10 lbs. pressure in the jacket for 4 hours, the alcohol

* Either shellac or lac obtained by extracting kiri with alcohol may be used.

being distilled and recovered through a water-cooled condenser as the reaction proceeds. Towards the end of distillation, vacuum is employed to effect a more complete recovery of the alcohol. The pasty mass in the still is taken out and kneaded in a mixing machine of the 'Universal' type under vacuum, the alcohol vapours being condensed and collected. The dried lumps are powdered to 60 mesh in a Christy and Norris disintegrator. The powder is finally dried in vacuum oven at 70° for 2 hours until the batch sample shows non-blistering and free flowing properties when moulded at $140-150^{\circ}$ and for $\frac{1}{2}$ to 3 minutes in the press. The powder is then stored in air-tight containers. The cost of manufacture of such a powder works out to be about $4\frac{1}{2}$ annas a pound using good quality shellac. If instead of shellac, lac recovered from *kin* is used, the cost is reduced to $3\frac{1}{2}$ annas per lb of moulding powder.

The 'wet process' described above for the manufacture of the moulding powder can be replaced by the 'dry process' recently investigated (*Indian Lac Research Institute Res. Note No. 25*). A considerable saving in the cost of equipment etc. is effected thereby.

From such moulding powders, electro-technical goods like switches, ceiling roses, wall plugs, junction boxes, etc. and general utility articles like soap and powder boxes, cigarette cases, buttons, boards, table-tops, pen and inkstands, etc. could be prepared. If, instead of using a fibrous filler, the resin varnish is applied to paper, mica or textile surfaces and several folds of them are compressed under the hydraulic press, very satisfactory and well polished laminated boards can be produced of diverse utility.

VARIATIONS OF UREA AND FORMALDEHYDE.

In the following experiments 200 g. of shellac and a similar quantity of wood flour were used and the powders dried for one hour at 90° but the quantities of urea and formaldehyde used were varied. The following results were obtained.

Wt. of urea.	Formalin (40% HCHO)	Impact strength (Cm kg /sq. cm.)	Heat stability (Marten's)
12 g.	37.0 c. c.	5.3	74°
18	56.0	5.45	74
24	75.0	5.9	72
30	94.0	6.0	80
40	125.0	5.6	75
50	150.0	5.8	76

It would appear from the above that the optimum proportion is 15% urea on the weight of lac or, assuming the mol. wt. of lac to be 1000, the following molecular proportions give the best results.

Lac	1 mol.
Urea	2.5 "
Formaldehyde	6.25 "

EFFECT OF VARYING THE AMOUNT OF FORMALDEHYDE.

It is apparent that 15% urea help to increase the heat-resistance but practical experiments show that urea lowers the plasticity, whilst formaldehyde works in the opposite direction. By using 15% urea on the weight of shellac and decreasing the proportion of formaldehyde, the following results were obtained.

No	Formalin	Impact strength (Cm. kg./sq. cm.)	Heat stability (Marten's).
1	94 c. c.	6.0	80°
2	47	6.0	79°
3	23.5	4.1	90°

Although it would seem from the above that by using only half the amount of formaldehyde the mechanical and thermal properties were not seriously affected, it was practically noted that powders 2 and 3 had extremely poor flow and produced articles without gloss and uniformity of surface appearance.

EXPERIMENTS WITH DIFFERENT FILLERS.

It is well known that moulded articles of widely differing mechanical and thermal properties can be prepared by variations in the nature and amount of fillers. The following results illustrate the range obtainable with a few selected fillers.

Organic fillers.

Type.	Filler. Percentage	Impact strength (Cm. kg./sq. cm.)	Heat stability (Marten's).
Wood flour	50	6.0	80°
Jute fibre	"	5.6	78
Cotton flock	"	8.8	81
Paper pulp	"	5.2	72

Mineral fillers.

Type	Filler Percentage	Impact strength (Cm. kg /sq. cm ,	Heat stability (Marten's)	Water absorption% 24 hours.
Slate dust	70	2.8	82°	0.09
Asbestos (fine)	"	2.2	88	0.09
" (fibrous)	"	3.4	90	0.09
Kaolin	"	4.3	80	0.11
Barytes	"	3.4	73	0.09

Among the fillers, cotton flock and asbestos (short fibres) appear to be the most useful. Wood-flour compositions have a moisture absorption of about 0.6 to 1.3% in 24 hours and other cellulosic fillers may be expected to have similar moisture absorption. Where the design of a particular article does not call for a high degree of strength, asbestos-filled articles would be preferable for better gloss, low moisture absorption and higher heat resistance.

SHELLAC-COALTAR AND SHELLAC-CASEIN MOULDING COMPOSITIONS.

Experiments have also been conducted with a view to finding cheaper materials which can replace either partly or wholly urea and formaldehyde used in the previous composition, thereby considerably reducing still the cost of the moulding powder. Shellac and coal-tar (*Indian Lac Research Inst., Res. Note, No. 23*), or its fractions and shellac and casein (*ibid.*, No. 21) have been combined with suitable accelerators and plasticisers to obtain compositions suitable for compression moulding. The articles made with shellac-coal tar compositions are black in colour and with shellac-casein any desirable colour can be obtained.

Besides casein, vegetable proteins obtained from Soyabean, Karanj cakes, etc. have also been successfully incorporated with shellac to obtain cheap moulding compositions suitable for preparing floor tiles, boards, etc.

INJECTION MOULDING.

Apart from the development of shellac moulding powders suitable for compression moulding described above, several other moulding compositions have been investigated for producing articles by the injection moulding process. The principle of injection moulding is, that the composition is fused in a heated barrel and the fused mass is squirted under pressure into a cold closed mould. The chief advantages of injection moulding over compression moulding are, (1) quicker output, (2) less wear on the moulds and (3) the possibility of more intricate mouldings. Among the synthetic resins that have attained commercial success are, cellulose acetate, styrol

compounds, acrylic acid resins, benzyl cellulose, etc. These resins are sold at Rs. 1/8/- to Rs. 3 per pound compared with thermo-hardening moulding powders selling at 8 to 12 annas per pound (pre-war rate).

A typical injection moulding composition from shellac recently developed at the Indian Lac Research Institute is described below :

Shellac (300 parts), jute (cut into short fibres, 200 parts), pigment (100 parts) and calcium stearate (9 parts) are mixed together and ground in a Christy and Norris disintegrator through a 20-25 mesh sieve. The powder, so obtained, is well kneaded with a solution containing formalin (100 parts), guanidin carbonate (15 parts) and water (500 parts). The well-kneaded mass is allowed to stand wet overnight and is then run between hot rollers where it dries and is obtained in the form of large sheets. These are allowed to cool, crushed to a coarse powder (5 to 10 mesh) and is directly used in the injection moulding press. The powder may be worked at a temperature of 125 to 135°. The heat resistance of articles, prepared by the process, is of the order of 70-80°, and the impact resistance is satisfactory.

Several kinds of articles like electrical switches, tumblers, bottle caps, buttons, etc. have been prepared at the Indian Lac Research Institute by injection moulding. These have been well received by the market. The high rate of production of injection moulded articles together with their lower costs is a distinct economic feature. For example, in a single impression switch mould, the rate of production was actually found to be as high as 215 pieces per hour.

RESINS FROM OIL.

The use of vegetable and fish oils, particularly the drying oils for varnishing purpose, is well known and researches on the improvement in the processes are being continually undertaken all over the world. Their use, however, as a plastic resin is of recent origin. A most striking effort in this direction is that of Dr. Goswami at the University College of Science, Calcutta, who has been able to convert all oils in succession into waxy and resinous products by the help of sulphurous and metallic oxides as catalysts under autoclave pressure. No details of the process are as yet known, but from a meagre statement appearing in magazines it is found that the waxes soften between 60° and 90° and that the resins at 100-130°. The resins are thermoplastic but treatment with a little alum followed by vacuum heating makes them thermo-hardening. Thus modified, they can be moulded with 50% wood flour at 200°. The yield of the resin is quantitative and all kinds of oils and fats, vegetable, animal and marine, can be used. The

discoverer proposes the name "Toilaj" for the plastic, and has already taken out English and Indian Patents.

It is claimed that moulding powders could be produced from this oil resin at 1 to 1½ annas per pound. If the claims can be commercially tested, the process can be considered as a new start in the field of natural or quasi-synthetic plastics.

Whilst the valuable properties of oil resins have made them indispensable in the arts and industries, their use as plastics in combination with shellac has been engaging the attention of workers at the Indian Lac Research Institute. A very interesting observation has been made by Sivaramakrishnan and Venugopalan that when cashewnut shell oil is compounded with shellac (with which it is compatible) resins of varying hardness are obtained according to the proportions of the ingredients used. The films obtained with such compositions are extremely water-resistant and elastic. Modification of such compounded resins with formaldehyde, furfural, acetaldehyde, urea, etc. show excellent promise for supplying a basic resin for the plastic and varnish industries. The presence of the phenolic group in the cashew oil offers greater flexibility in condensation reactions, and the cheap availability of this raw material is expected to exercise an important influence in the natural plastic industry.

MODIFICATION OF SHELLAC WITH FORMALDEHYDE, FURFURALDEHYDE AND ANILINE.

Improved shellac compositions of low acidity for preparing varnishes and polishes of heat and water resistant type are obtained by condensing shellac with suitable proportions of aniline in presence of solvents like acetone, methyl ethyl ketone, etc. A typical composition is prepared as follows :—

100 Grams lac (shellac) are refluxed with 25 c.c. of formalin (40%) over an oil-bath at 120° for 1 hour. The resin formed is then dissolved in 150 c.c. of acetone and 18 c.c. of aniline are gradually added. The whole is then refluxed over a water-bath for 3-4 hours. The resin solution, thus obtained, after dilution with alcohol is used as varnish for coating on metals, wood, etc. Heat and water resistance of the films can be considerably improved by baking at 100-120° for about half an hour.

The resin solution, obtained above, when mixed with suitable plasticisers and fillers like wood flour, jute, asbestos, etc. gives very good thermoplastic moulding compositions which can be used for injection moulding.

COMPOSITION OF PRUSSIAN AND TURNBULL'S BLUES. PART IV. STUDY OF THEIR ADSORPTIVE PROPERTIES.

BY ABANI K. BHATTACHARYA.

Studies on the adsorption of ferrocyanogen and ferric radicals by Prussian blue, and of ferrous and ferricyanogen radicals by Turnbull's blue have been carried out. Evidence has been produced to show that in some cases chemical action and in some cases negative adsorption may take place.

In a previous paper (*Z. anorg. Chem.*, 1933, **213**, 240) the analytical results of various samples of Prussian and Turnbull's blues, prepared by mixing the reactants in different proportions and concentrations, have produced evidence of the possibility of adsorption of different groups or radicals in course of precipitation. A detailed study of the phenomenon has, therefore, been carried out by a series of experiments and their results discussed in this paper.

EXPERIMENTAL.

Solutions of ferric chloride and potassium ferrocyanide of known strengths were mixed together in equivalent proportion to precipitate a calculated amount of Prussian blue. The precipitate was thoroughly washed free from electrolytes and suspended in boiled distilled water, the total volume being made up to a litre. The precipitate was then vigorously shaken to make the suspension uniform as far as possible, before using the suspension for adsorption experiments. 10 C.c. of this suspension were quickly withdrawn and transferred into several flasks arranged in succession. Gradually increasing amounts of the salt, whose adsorption had to be determined, were added to the blue precipitate and the total volume of the mixture was made up to 100 c.c. in each case, and left overnight to settle. If on adding the salt solution the blue precipitate assumed a colloidal form, about 2 to 3 g. of ammonium chloride were added to coagulate it, and then the equilibrium concentration was determined by withdrawing 5 to 10 c.c. of the clear supernatant solution.

For Turnbull's blue the same procedure was adopted.

The equilibrium concentration of ferric chloride was estimated gravimetrically as Fe_2O_3 ; those of ferrous sulphate and potassium ferrocyanide were determined by titrating against $N/200\text{-KMnO}_4$ solution; while that of potassium ferricyanide was estimated by iodometry where the liberated iodine from potassium iodide was titrated against $N/200\text{-sodium thiosulphate}$ solution.

On the basis of these estimations the adsorptive properties of various samples of Prussian and Turnbull's blues have been studied. In some cases negative adsorption has also been observed. By extrapolation it has been possible, further, to observe some cases of adsorption which are followed by chemical changes, after a certain amount of the adsorbent had been added to the Prussian or Turnbull's blue.

DISCUSSION.

From the curves it follows apparently that some samples of Prussian and Turnbull's blues at first display a tendency of adsorption which is later disturbed by the effects of chemical reaction between the adsorbent and the adsorbate.

FIG. 1.

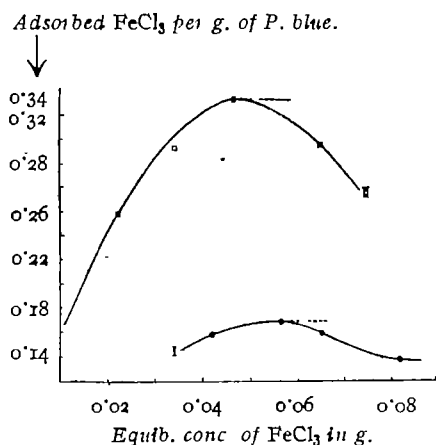
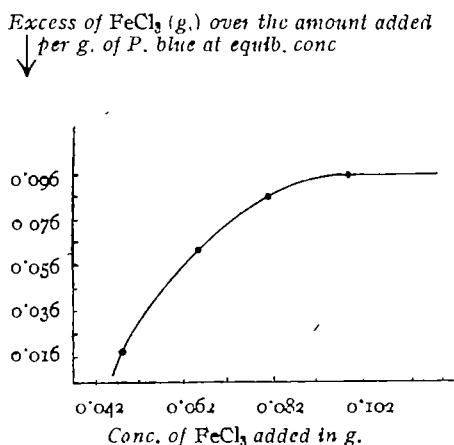


FIG. 2 (Curve III).

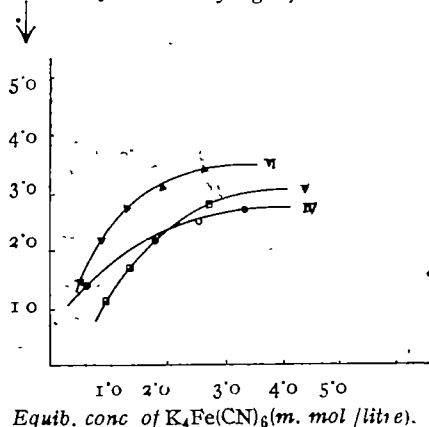


Curves I and II refer respectively to P. blues obtained by mixing (i) FeCl_3 and $\text{K}_4\text{Fe}(\text{CN})_6$ in equiv. proportion and (ii) 1 equiv. of FeCl_3 with $3/2$ equiv of $\text{K}_4\text{Fe}(\text{CN})_6$.

Curve III refers to P. blue prepared as in Curve II Fig. 2

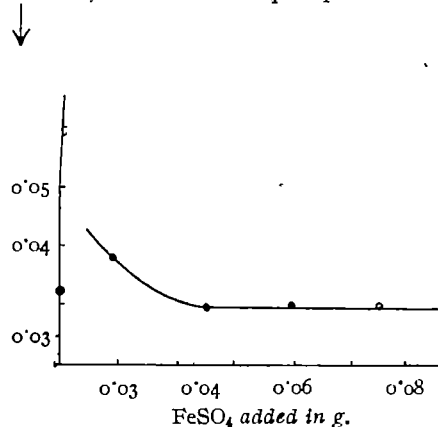
Curves I, II, VIII and X lend support to the view that adsorption and chemical oxidation-reduction are both responsible for the final composition of Prussian and Turnbull's blues; hence the percentage composition of the various samples vary considerably with the proportion and concentration of the reactants mixed together as communicated in a previous publication (*loc. cit.*).

FIG. 3.

 $K_4Fe(CN)_6$ adsorbed by 1 g. of P. blue.

Curves IV-VI refer respectively to P. blue prepared by mixing $FeCl_3$ and $K_4Fe(CN)_6$ in (i) equiv. proportion, (ii) $1 : 3/2$, (iii) $3/2 : 1$.

FIG. 4 (Curve VII).

Excess of Fe calc. as $FeSO_4$ at equib. conc.

Curve VII refers to $FeSO_4$ added over the amount added to T. blue prepared by mixing $FeSO_4$ and $K_4Fe(CN)_6$ in equiv. proportion.

Curve VII definitely suggests that a chemical action takes place between acidified ferrous sulphate and the precipitate of Turnbull's blue, formed by mixing the reactants in equivalent proportion. The results of adsorption experiments lend further support to the view, previously communicated, that during the precipitation of Turnbull's blue, by mixing an acidified solution of ferrous sulphate with potassium ferricyanide, the role of chemical change is much greater than adsorption. This is why a negative adsorption has been observed. The curve shows that after a certain concentration of ferrous sulphate, the limit of chemical change as well as that of adsorption has been reached. With increasing quantities of ferrous sulphate added to 10 c.c. of the suspension containing 0.1 g. of Turnbull's blue, the liberated amount of the reducing product of the reaction (calculated as ferrous sulphate in excess of the amount already added) at first decreased and then became constant. It seems from the curve that the reaction between the Turnbull's blue and ferrous sulphate was complete at a concentration of 0.304 g. per litre, while the adsorption of ferrous sulphate continued to increase till the concentration reached 0.456 g. per litre. The curve, therefore, runs down a short slope between the concentration-range of 0.304 to 0.456 g. of $FeSO_4$ per litre and then becomes parallel to the concentration axis.

Curve III shows that chemical action ultimately influences adsorption when gradually increasing quantities of ferric chloride are added to Prussian blue prepared by mixing $3/2$ equivalents of ferric chloride with one

equivalent of potassium ferrocyanide. The negative adsorption observed in this case seems to be due to the fact that Prussian blue prepared with excess of ferric chloride retains already enough of it through adsorption, so that with further quantities of ferric chloride gradually added, the limit of adsorption is surpassed and chemical action sets in. Hence the excess of iron compound, calculated as FeCl_3 released by Prussian blue on adding increasing amounts of ferric chloride, tends to reach a certain maximum beyond which the curve becomes almost parallel to the concentration axis of FeCl_3 .

Curve IV is an adsorption curve showing that Prussian blue prepared by mixing the reactants in equivalent proportion adsorbs increasing quantities of potassium ferrocyanide up to a certain limit on adding gradually increasing amounts of the latter. Similar results are shown by the adsorption curves V and VI where the Prussian blues have been prepared by mixing (i) one equivalent of ferric chloride with $3/2$ equivalents of potassium ferrocyanide, and (ii) $3/2$ equivalents of ferric chloride with one equivalent of potassium ferrocyanide respectively. Such observations support the formation of adsorption compounds, which depends of course, on the conditions of precipitation and formation of the blue.

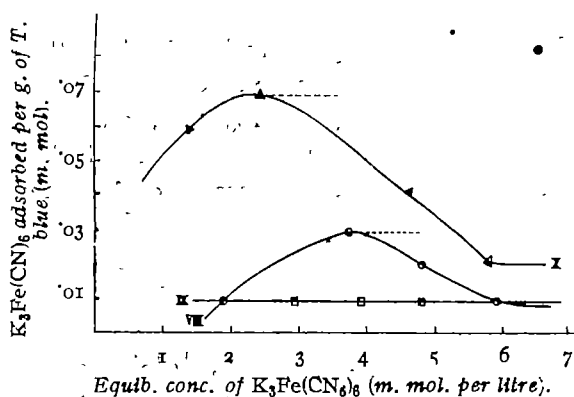
It will be observed, further, that the sample of Prussian blue prepared by mixing excess ($3/2$ equivalents) of ferric chloride adsorbs more of potassium ferrocyanide than that which was prepared by mixing ferric chloride and potassium ferrocyanide in equivalent proportions. Likewise, a sample prepared by mixing $3/2$ equivalents of potassium ferrocyanide adsorbs much less of this salt than one prepared by mixing the reactants in equivalent proportions. These results are quite in conformity with the laws of adsorption.

In curve I the ferric chloride is adsorbed up to a certain concentration after which the amount adsorbed slowly decreases with increasing concentrations of ferric chloride indicating the disturbance of adsorption phenomenon by the chemical action after a certain quantity of the adsorbate has been added. Curve II leads to a similar inference. In this curve, the phenomenon of adsorption goes up to a much higher concentration of ferric chloride, in as much as the sample of this blue was prepared by adding excess ($3/2$ equivalents) of potassium ferrocyanide, while the sample in curve I was prepared by mixing the reactants in equivalent proportion. These results are in conformity with the adsorptive properties of substances.

Curve VIII shows that in Turnbull's blue, prepared by mixing the reactants in equivalent proportion, adsorption of potassium ferrocyanide takes place up to a certain extent, when the chemical action starts and

goes a greater length than that of Prussian blue with ferric chloride. From curve IX it is evident that when Turnbull's blue is prepared by mixing one equivalent of ferrous sulphate with $3/2$ equivalents of potassium ferricyanide, its adsorptive capacity as well as its chemical reactivity towards the latter are almost or completely exhausted. Hence the curve is a line parallel to the equilibrium concentration axis.

FIG. 5.



Curves VIII-X refer respectively to T. blue prepared by mixing $FeSO_4$ and $K_3Fe(CN)_6$ as (i) 1 : 1, (ii) 1 : $3/2$, (iii) $3/2$: 1.

Curve X shows that the adsorption of $K_3Fe(CN)_6$ is much greater with Turnbull's blue prepared by mixing $3/2$ equivalents of ferrous sulphate than that which had been prepared by mixing one equivalent of ferrous sulphate. This is quite usual in view of the fact that in the former sample, much greater amount of ferrous sulphate remains adsorbed than in the latter. The steep course of curve X further indicates the avidity between the adsorbed Fe and potassium ferricyanide.

While discussing the analytical results of the various samples of Prussian and Turnbull's blues in the previous communication, already referred to, the rôle of selective adsorption of Fe^{++} , Fe^{+++} , $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ was observed to be very important in determining the final composition of these compounds. The adsorption curves also lead to a similar conclusion and confirm the view that Prussian blue has a much greater adsorptive power for ferric and ferrocyanogen radicals than Turnbull's blue prepared under similar conditions.

Author's thanks are due to Dr. N.R. Dhar and Dr. S. Ghosh of the Allahabad University for the great interest they have taken in these investigations.

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Received September 9, 1940.

STUDIES IN THE CAMPHOR SERIES PART VI.

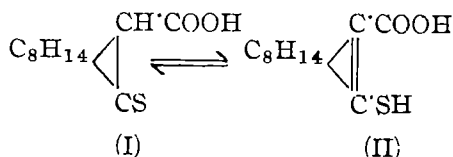
BY DINESH CHANDRA SEN.

Thiocamphor- α -carboxylic acid, thiocamphor- α -dithiocarboxylic acid and oxymethylene-thiocamphor have been prepared by the action of carbon dioxide, carbon disulphide and formic ester respectively on sodiothiocamphor. The constitution of these compounds has been established and a few derivatives described

Sodiothiocamphor has been utilised for the synthesis of isonitrosothiocamphor, bithiocamphor and alkylidene thiocamphors (Sen, *J. Indian Chem. Soc.*, 1935, **12**, 751; 1936, **13**, 523; 1937, **14**, 216 etc.). In the present communication the behaviour of carbon dioxide, carbon disulphide and formic ester towards sodiothiocamphor has been described.

When a current of dry carbon dioxide is passed through sodiothiocamphor in benzene-ether medium at 0°, thiocamphor- α -carboxylic acid is obtained as the sodium salt from which the acid can be isolated. *l*-Thiocamphor gives *d*-thiocamphor- α -carboxylic acid, m.p. 125°, $[\alpha]_D^{30}$, 21.03° and *dl*-thiocamphor similarly yields *dl*-carboxylic acid, m.p. 121°. These are fairly stable β -thioketonic acids none of which has hitherto been isolated in the free state. These acids lose carbon dioxide and give the corresponding thiocamphor (*l*- and *dl*- respectively) on distillation in vacuum, a property also shared by their oxygen analogues (*cf.* Bruhl, *Ber.*, 1904, **37**, 2074; *Z. physikal. Chem.*, 1900, **34**, 1; Oddo, *Gazzetta*, 1893, **23**, 1, 74; Haller, *Compt. rend.*, 1886, **102**, 1477; Bredt and Sand Kuhl, *Annalen*, 1909, **366**, 11, etc.).

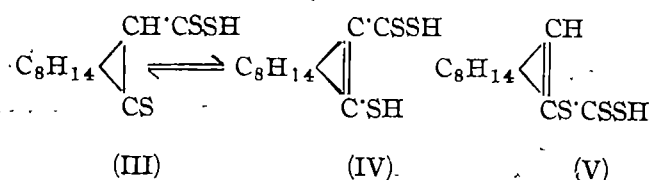
The colour of the acids (white) as well as their capacity to form yellow lead salts suggest the existence of these acids in the thiol phase. Formation of a blue colour with ferric chloride (aqueous alcoholic), however, indicates thio-thiol tautomerism of the acids,



which also offers an explanation of mutarotation of *d*-thiocamphor-carboxylic acid, $[\alpha]_D^{30}$, 21.03° (in benzene) falling down to $[\alpha]_D^{30}$, 19.56° after 24 hours.

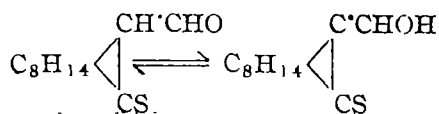
Thiocamphor-carboxylic acid cannot be esterified by the usual method of esterification with alcohol and hydrogen chloride but it gives a methyl ester when methyl iodide acts on the silver salt of the acid. The ester, like the acid shows thio-thiol tautomerism (ferric chloride colouration).

Thiocamphor-dithiocarboxylic acid is obtained by the interaction of dry carbon disulphide and sodiothiocamphor in benzene. The acid is very slowly affected by semicarbazide but when treated with bases like ethylamine, phenylhydrazine etc. sulphuretted hydrogen is readily evolved. When distilled in vacuum it gives carbon disulphide and thiocamphor (*cf.* Tschugaelf and Pigoulewski, *Compt. rend.*, 1911, **163**, 388). The analogous behaviour of thiocamphor-dithiocarboxylic acid and camphor-dithiocarboxylic acid and the evolution of hydrogen sulphide with organic bases suggest the formula (III) for the acid. The formation of a deep blue colour with ferric chloride suggests thio-thiol tautomerism, which eliminates the possibility of its being a thioxanthic acid (V).



Methyl thiocamphor- α -dithiocarboxylate has been obtained by treatment of sodiothiocamphor in benzene successively with carbon disulphide and dimethyl sulphate, as a light yellow liquid which also gives a blue colour with ferric chloride.

By the condensation of formic ester with sodiothiocamphor, oxymethylenethiocamphor is formed as a light brown liquid which is a strongly acidic substance. It gives a brown copper salt, a yellow mercuric salt, a red colouration with ferric chloride which slowly changes to green and it forms a semicarbazone identical with that of oxymethylenecamphor (*cf.* Wallach and Steindorff, *Annalen*, 1903, **329**, 129). These properties suggest the following structures for oxymethylenethiocamphor (*cf.* Bishop, Claisen *et al.*, *Annalen*, 1894, **281**, 330; Bredt *et al.*, *ibid.*, 1919, **366**, 62; Brühl, *Ber.*, 1904, **37**, 2074, etc.).



E X P E R I M E N T A L.

Thiocamphor- α -carboxylic Acid.—Sodiothiocamphor was prepared by the usual method in benzene medium. The benzene solution was diluted with ether and a current of carbon dioxide was passed through the solution for 12 hours at 0° and then for 6 hours at the room temperature (39°). The resulting gelatinous mass was poured on to crushed ice and the benzene-ether layer containing unchanged thiocamphor was separated. The aqueous solution was extracted once with ether and then acidified with dilute hydrochloric acid at 0° . An oil separated out which slowly solidified to a colourless solid. It was redissolved in sodium carbonate solution, filtered and reprecipitated with dilute hydrochloric acid. The precipitate on recrystallisation from a mixture of alcohol and ether gave thiocamphor- α -carboxylic acid as colourless hexagonal plates, m.p. 125° , yield 30%, $[\alpha]_D^{30} + 21.03^\circ$ which falls to $[\alpha]_D^{30} + 19.36^\circ$ after 24 hours (in benzene). (Found: C, 62.64; H, 7.61; Equiv., 211.1. $C_{11}H_{16}O_2S$ requires C, 62.26; H, 7.55 per cent. Equiv., 212).

The *dl*-thiocamphor- α -carboxylic acid, m.p. 121° , was similarly prepared from the sodio derivative of *dl*-thiocamphor. (Found: C, 62.27; H, 7.68; Equiv., 210. $C_{11}H_{16}O_2S$ requires C, 62.26; H, 7.55; Equiv., 212).

These acids are readily soluble in alkalis giving colourless solutions and in organic solvents giving light pink solutions. They give blue colouration with ferric chloride in aqueous alcoholic solutions. The *semicarbazone* crystallised from alcohol as colourless needles, m.p. $133-34^\circ$. It is identical with the semicarbazone from *d*-camphor- α -carboxylic acid (mixed m.p.). (Found: N, 16.80. Calc. for $C_{12}H_{16}O_3N_2$: N, 16.60 per cent).

l-Thiocamphor from *d*-Thiocamphor- α -carboxylic Acid.—*d*-Thiocamphor- α -carboxylic acid (5 g.) was distilled in vacuum when *l*-thiocamphor sublimed over at $95-100^\circ/5$ mm. as a silky orange crystalline substance which was purified by resublimation, yield 3.5 g. *l*-Thiocamphor (m.p. 146°), thus obtained, has $[\alpha]_D^{30} - 24.58^\circ$ (in benzene) and $[\alpha]_D^{30} - 12^\circ$ in ethyl acetate. Thiocamphor, like camphor, thus gives different values for specific rotations in different solvents. (Found: S, 19.17. Calc. for $C_{10}H_{16}S$: S, 19.05 per cent).

Methyl thiocamphor- α -carboxylate was obtained by converting the acid into its silver salt and treating the yellow silver salt with methyl iodide. The silver salt from thiocamphor (2 g.), prepared in the usual way, was washed with alcohol and ether, dried and then refluxed with methyl iodide (5 g.) for 2 hours at 80° . The solution was then cooled, filtered, ether removed

and the residue on crystallisation from alcohol gave the ester as colourless needles, m.p. 96° , yield 1.8 g. It gave a blue colour with aqueous alcoholic ferric chloride. (Found: C, 63.85; H, 7.98; M.W., 228. $C_{12}H_{14}O_4S$ requires C, 63.71; H, 7.96 per cent. M. W. 226).

d-Thiocamphor- α -dithiocarboxylic Acid.—Thiocamphor (10 g.) was converted in benzene into the sodio derivative and treated with dry carbon disulphide (10 c.c.) at 0° . After 1 hour, the mixture was refluxed at 80° for 2 hours. It was then cooled, mixed with ice-cold water and extracted with ether. The yellow aqueous solution was cooled to 0° and slowly acidified with dilute hydrochloric acid. A red offensive smelling oil separated out which on keeping for 2-3 days gave a solid which was washed with alcohol to remove the adhering oil. It crystallised from petroleum ether (b.p. $40-50^{\circ}$) as brown needles, m.p. 172° . It is moderately soluble in alcohol and petroleum ether and readily soluble in ether, benzene and chloroform. It gives a blue colour with aqueous alcoholic ferric chloride. It has got a strong mercaptanic smell. The alcoholic solution is deep brown having a green fluorescence. It is *dextrorotatory*, $[\alpha]_D^{30} + 58.03^{\circ}$ in 1% benzene solution. (Found: C, 53.97; H, 6.65; S, 39.45; M.W., 248. $C_{11}H_{16}S_2$ requires C, 54.10; H, 6.56; S, 39.34 per cent. M.W., 244). The *semicarbazone* crystallised from alcohol as light yellow needles, m.p. 165° . (Found: N, 14.56. $C_{12}H_{16}ON_2S_2$ requires N, 14.74 per cent).

Methylthiocamphor- α -dithiocarboxylate.—Sodio thiocamphor was treated with sodium-dried carbon disulphide at 0° , and then with methyl sulphate. After heating at 100° for 2 hours, the mixture was treated with ice-cold water and extracted with ether. The ethereal solution was dried, evaporated and the residual liquid on distillation gave the ester as a light yellow liquid, b. p. $80^{\circ}/10$ mm., having slight mercaptanic smell; yield 20 per cent. The compound gives a blue colour with aqueous alcoholic ferric chloride. On keeping it decomposes developing a very strong mercaptanic odour. (Found: C, 55.98; H, 7.02; S, 37.52. $C_{12}H_{16}S_2$ requires C, 55.81; H, 6.98; S, 37.21 per cent).

Oxymethylenethiocamphor.—*l*-Thiocamphor (10 g.) in benzene solution was converted into sodio derivative by molecular sodium, and dry formic ester (6 g.) was added at 0° . After 12 hours, the mixture was poured into crushed ice and the benzene layer after drying over anhydrous sodium sulphate was evaporated. The residual yellow viscous mass was dissolved in alcohol and treated with an aqueous solution of copper acetate, when the dark brown copper salt was precipitated, which crystallised from alcohol as dark brown needles, m.p. $154-55^{\circ}$ (decomp.). [Found: S, 13.92; Cu, 14.33. $(C_{12}H_{16}O_2S_2)Cu$ requires S, 14.11; Cu, 14.02 per cent].

When the alcoholic solution of oxymethylenethiocamphor was treated with mercuric chloride, the mercury salt was obtained which crystallised from alcohol as yellow, silky, prismatic needles, m.p. 125° , $[\alpha]_D^{30}$, $+22.22^{\circ}$ (in benzene). (Found: Hg, 34.10; M.W. 596. $C_{22}H_{30}O_2S_2Hg$ requires Hg, 33.90 per cent. M.W., 590).

The mercury salt was suspended in alcohol and was freed of mercury by hydrogen sulphide. The alcoholic filtrate was diluted with water and the resulting oil was extracted with ether. The ethereal solution gave oxymethylenethiocamphor as a light brown liquid, b.p. $110-15^{\circ}/5$ mm., yield poor. It is a strongly acidic liquid, readily soluble in sodium carbonate and bicarbonate solutions. It is very unstable. The freshly distilled liquid is light brown, but in the course of a few hours it becomes dark brown and viscous. (Found: C, 67.38; H, 8.22; S, 16.35; M. W., 198. $C_{11}H_{16}OS$ requires C, 67.35; H, 8.16; S, 16.33 per cent. M. W., 196). The *semicarbazone* crystallised from alcohol as colourless needles, m. p. $217-18^{\circ}$. It is identical with the semicarbazone derived from oxymethylenecamphor. (Found: N, 17.83. Calc. for $C_{12}H_{18}O_2N_3$: N, 17.72 per cent).

My thanks are due to Dr. P. K. Bose for his kind interest in this investigation and for the facilities of his laboratory.

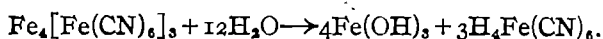
COMPOSITION OF PRUSSIAN AND TURNBULL'S BLUES.

PART V. ROLE OF HYDROLYSIS AND THEIR COMPOSITIONS.

BY ABANI K. BHATTACHARYA.

It has been observed in several samples of Prussian and Turnbull's blues, prepared under wide range of dilutions of the mixed reactants at a definite temperature that the composition of Prussian blue is much affected by its hydrolysis, while Turnbull's blue is much less affected, because of the presence of an excess of acid in ferrous sulphate. By extrapolation of the values of CN/Fe against the dilutions of the mixed constituents, a probable ratio of Fe:CN for Prussian and Turnbull's blues of identical composition has been obtained.

It was suggested in a previous publication (*Z. anorg. Chem.*, 1933, 213, 240) that the composition of Prussian and Turnbull's blues may be slightly changed through hydrolysis of the precipitated product during repeated washing, or during long dialysis inside a parchment bag. It had also been reported by Ghosh, Dhar and others (*J. Phys. Chem.*, 1925, 29, 659) that colloidal Prussian blue gets partially hydrolysed during dialysis and ageing and produces some ferric hydroxide according to the reaction,



With a view to studying how far the composition of these blues is altered or influenced by the dilution of iron and ferrocyanogen salts, several samples of Prussian and Turnbull's blues were prepared under a wide range of dilution of the mixed reactants at a definite temperature and the analytical results have been discussed in this paper.

EXPERIMENTAL.

Solutions of ferric chloride, potassium ferrocyanide, ferrous sulphate, and potassium ferricyanide of concentrations $M/5$, $M/10$ and $M/100$ were prepared and samples of Prussian and Turnbull's blues were prepared by mixing the corresponding iron and ferrocyanogen salts at each of the above concentrations in equivalent proportion. The samples were thoroughly washed free of soluble impurities, as far as possible, and their compositions determined by estimating the total iron and cyanogen radical per 100 g. of the substance.

Ferric chloride was prepared in pure distilled water while ferrous sulphate had to be acidified with dilute sulphuric acid to prevent its

hydrolysis and consequent oxidation by atmospheric oxygen. The blue precipitates were filtered free from soluble impurities as far as possible and dried by means of an air-oven in Buchner funnels. The precipitates, when dry, were finely powdered in an agate mortar and preserved in dry and clean tubes for analysis.

TABLE I.
Prussian blue.

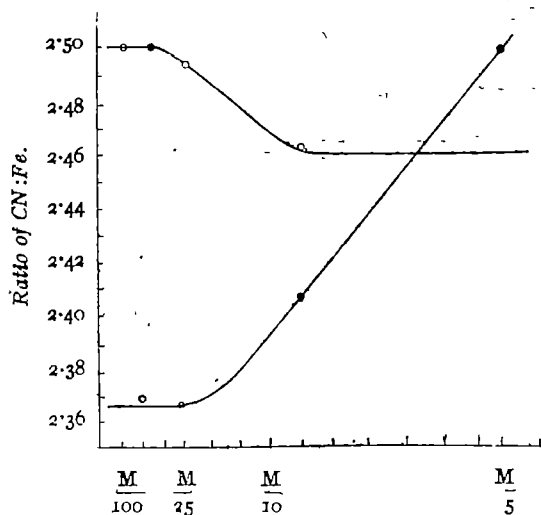
Temp. = 35°.

Conc. of FeCl_3	Conc. of $\text{K}_4\text{Fe}(\text{CN})_6$	Total Fe.	Total (CN).	Fe:CN.
M/5	M/5	32.820%	38.075%	1:2.50
M/10	M/10	35.245	39.530	1:2.41
M/25	M/25	33.790	37.140	1:2.368
M/50	M/50	37.050	40.830	1:2.373

TABLE II.
Turnbull's blue.

Temp. = 35°.

Conc. of FeSO_4	Conc. of $\text{K}_3\text{Fe}(\text{CN})_6$	Total Fe.	Total (CN).	Fe:CN.
M/5	M/5	32.08%	36.64%	1:2.46
M/10	M/10	32.01	36.60	1:2.46
M/25	M/25	30.86	35.54	1:2.49
M/50	M/50	31.20	36.23	1:2.50
M/100	M/100	30.42	35.34	1:2.50

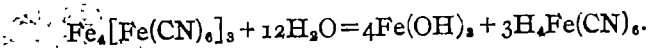


Conc. of reactants.

DISCUSSION.

From the foregoing tables and the curves drawn by extrapolating the values of CN/Fe against the concentrations of the reactants, mixed together for preparing the blues, it will be evident that the compositions of the Prussian and Turnbull's blues are undoubtedly affected by the dilution of the reacting solutions. It has already been discussed in previous communications that the phenomena of hydrolysis and of adsorption, together, have some influence on the composition of these blues; this will be supported from the order of change in the ratio of Fe:CN that takes place with the dilution of the reactants. The solution of ferrous sulphate being acidic due to the presence of dilute sulphuric acid, effects of hydrolysis will evidently be much less in the case of Turnbull's blue. In the preparation of Prussian blue, aqueous solutions of ferric chloride and potassium ferrocyanide were mixed together, and hence hydrolysis was relatively more marked in this case than in the case of Turnbull's blue.

From the observations recorded in Table I, sufficient support to our views regarding the influence of hydrolysis on the composition of Prussian blue has been obtained. Gradually the ratio CN:Fe diminishes as the dilutions are increased, which shows that iron, as ferric hydroxide, adds to the total iron content of the compound, although a part of the cyanogen may be lost as soluble $H_4Fe(CN)_6$ according to



The above equation further suggests that more of Fe as $Fe(OH)_3$ is retained by the compound than what is lost by it as soluble $H_4Fe(CN)_6$.

In Table II the observations are otherwise. The ratio of Fe:CN gradually decreases with dilution and tends to reach a limit (1:2.5) at higher dilution. In the case of Prussian blue, too, the limiting value of Fe:CN (1:2.37) is reached at higher dilution. When the curves are drawn on the same scale, it is further observed that the compositions of Prussian and Turnbull's blues are probably identical at such concentration of the respective reactants as is represented by the point of intersection of the two curves. In Table I, the value of Fe:CN at concentration $M/5$ is 1:2.5, while the value of Fe:CN at concentration $M/10$ is 1:2.41. It is likely, therefore, that at a concentration of the respective reactants between $M/5$ and $M/10$, say at about $M/8$, the ratio of Fe:CN would be equal to 1:2.465 as can be guessed from the point of intersection of the two curves, provided, of course, the conditions of dilution and temperature could be maintained identical in each case.

In view of the above results, it may be inferred that Prussian and Turnbull's blues tend to assume identical composition, but the secondary effects, which are of a chemical and adsorptive nature, do not allow us to determine either the exact condition, or the ratio of Fe:CN for an absolutely identical compound. It can, however, be guessed by extrapolation, that the ratio of Fe:CN would be equal to 1:2.46 at a dilution of about $M/8$ of the mixed constituents, under such conditions as were maintained during the author's investigations; and this goes to confirm the author's view regarding the influence of dilution on the compositions of Prussian and Turnbull's blues.

Thanks are due to Dr. N. R. Dhar and Dr. S. Ghosh of the Allahabad University for their kind interest and guidance in this work.

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Received September 26, 1940.

COMPOSITION OF PRUSSIAN AND TURNBULL'S BLUES.

PART VI. MAGNETIC SUSCEPTIBILITY OF THE COMPOUNDS.

BY ABANI K. BHATTACHARYA.

Magnetic susceptibility of various samples of Prussian and Turnbull's blues have been determined and the P_{Weiss} values were found to be roughly ranged between 20 and 21 P_{Weiss} magnetons, although their calculated values were 16.5 and 19.6 respectively. The aged samples of Prussian and Turnbull's blues gave much closer P_{Weiss} values showing that, on ageing, they become more identical in composition. Slight variations by changing the concentration of the respective reactants have been attributed to the influence of adsorption on the composition of the sols.

Welo and Baudisch (*Nature*, 1925, **116**, 606) who have considered the collected data due to Rosenbohm (*Z. physikal. Chem.*, 1919, **98**, 693) and made some new measurements of the susceptibilities of certain complex cyanides and related compounds of iron, suggested that a complex ion, whose effective atomic number equals that of an inert gas, should manifest diamagnetic properties, even though the central atom of the complex possesses a strongly paramagnetic susceptibility value as an individual ion.

The effective atomic number is calculated after Sidgwick on the basis that each co-ordinated unit in the complex is bound to the central atom by electron-sharing bonds. Thus, iron in ferrocyanogen complex, $[\text{Fe}(\text{CN})_6]^{4-}$, with an effective atomic number of 36 is diamagnetic, whereas in ferricyanogen complex with an effective atomic number of 35, it is paramagnetic having a value of $P_{\text{Weiss}} = 10$.

In the determination of the magnetic susceptibility of Prussian and Turnbull's blues in their pure state as ferric ferrocyanide $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ and ferrous ferricyanide $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ respectively, the theoretically calculated value would be 116 Weiss magnetons per gram molecular weight, or $116/7 = 16.6$ (approx.) per gram atom of Fe in Prussian blue, and 98 Weiss magnetons per gram molecular weight, or $98/5 = 19.6$ Weiss magnetons per gram atom of Fe in Turnbull's blue.

EXPERIMENTAL.

Prussian and Turnbull's blues were prepared by mixing the respective reactants in equivalent proportion. The samples so prepared were washed free of soluble impurities as far as possible and dried in hot air. A few samples were also dried in the sun. Such samples, as were prepared by

mixing an excess of potassium ferrocyanide, were dialysed till free from the soluble impurities, and the dialysed sol was dried by slow evaporation. In the case of aged samples the reactants were mixed and kept in the mixed condition for several weeks, and then filtered and dried. All the samples were individually estimated for Fe_2O_3 and the percentage of total Fe present in each was determined.

The magnetic susceptibility of these samples per gram of iron was determined by means of a Curie's balance. Anhydrous cobalt sulphate was used as a standard substance. The magnetic susceptibility was calculated from the formula,

$$P_{\text{weiss}} = 14 \cdot 04 \sqrt{\chi_M \cdot M \cdot T}$$

where χ_M = susceptibility per gram, and M = mol. wt. [here, M = that weight of the substance which contains one gram atom of Fe]. Knowing that $59 \cdot 7 \times 10^{-6}$ = mass susceptibility of anhydrous CoSO_4 , the paramagnetic susceptibility of the substance,

$$P_{\text{weiss}} = 14 \cdot 07 \sqrt{\chi_M \cdot M \cdot T}$$

where M is that weight of the substance which contains one gram atom of Fe and T is the absolute temperature, and $\chi = \frac{59 \cdot 7 \times 10^{-6} \times \theta}{\phi}$, θ and ϕ being the mass deflections of the substance and anhydrous cobalt sulphate respectively.

TABLE I.

Weiss magneton values of Prussian and Turnbull's blues prepared by mixing the reactants of equal concentrations and in equivalent proportion.

Conc. of the reactants.	P_{weiss} values for blues		Conc. of the reactants.	P_{weiss} values for blues	
	Prussian.	Turnbull		Prussian.	Turnbull.
$M/5$	21.54	21.47	$M/25$	19.84	20.85
$M/10$	20.39	21.28	$M/50$	19.45	21.67
$M/20$	20.89	21.35	$M/100$	19.52	21.47

TABLE II.

P_{weiss} values of the Prussian and Turnbull's blues prepared by ageing the mixture of the reactants along with the precipitate of the blues; the reactants being mixed in equivalent proportion at several concentrations.

Conc. of the reactants.	P_{weiss} values for blues		Conc. of the reactants.	P_{weiss} values for blues	
	Prussian.	Turnbull.		Prussian.	Turnbull.
$M/5$ with $M/5$	20.90	20.93	$M/20$ with $M/5$	20.18	21.60
$M/20$ „ $M/20$	21.10	21.38	$M/5$ „ $M/40$	20.22	21.08
$M/5$ „ $M/20$	20.60	21.10	$M/40$ „ $M/5$	19.56	21.71

TABLE III.

P_{Weiss} values of Prussian blues prepared by mixing the reactants at unequal concentrations.

Conc. of the reactants $\text{FeCl}_3\text{--K}_3\text{Fe}(\text{CN})_6$	Proportion of mixing.	P_{Weiss} values.
$M/5$ with $M/2.5$	1 equiv. with 1 equiv.	19.95
$M/10$ „ $M/2.5$	„ „	19.12
$M/2.5$ „ $M/20$	„ „	19.57
$M/20$ „ $M/2.5$	„ „	18.87
$M/3.24$ „ $M/2.30$	1 equiv. FeCl_3 with 5/9 equiv. $\text{K}_3\text{Fe}(\text{CN})_6$	17.55

TABLE IV.

P_{Weiss} values of Turnbull's blues prepared by mixing the reactants at unequal concentrations, proportion of mixing being 1 equiv. : 1 equiv.

Conc. of the reactants $\text{FeSO}_4\text{--K}_3\text{Fe}(\text{CN})_6$	P_{Weiss} values.
$M/5$ with $M/10$	20.58
$M/10$ „ $M/5$	20.22
$M/5$ „ $M/20$	19.64

DISCUSSION.

From the foregoing tables both Prussian and Turnbull's blues appear to have practically equal Weiss magneton values and the calculated figures from experimental observations approximately range between 20 and 21 Weiss magnetons per gram atom of Fe contained in the substance. From the magnetic additive relations, the Weiss magneton value for $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, per gram atom of Fe should be 16.5 and that of $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ should be 19.6. But the experimental values recorded in the above tables show a pretty wide discrepancy, particularly in the case of Prussian blue.

In the light of mutual oxidation and reduction phenomenon that may take place between the reactants, Weiss magneton values of Prussian and Turnbull's blues should be anywhere between 16.5 and 19.6. With the assumption that equal quantities of Prussian and Turnbull's blues are formed, P_{Weiss} values ought to have been the mean of 19.6 and 16.5 or equal to 18.05. The experimental figures are, however, much away, from 18.05, and hence no conclusion can be arrived at regarding the proportion of Prussian and Turnbull's blues formed in the compound.

The aged samples of Prussian and Turnbull's blues, however, give much closer P_{Weiss} values, which suggest that by ageing they tend to assume a more similar composition than the fresh ones. This is in support of our

views already advanced on the basis of analytical results (*Z. anorg. Chem.*, 1933, **213**, 242).

P_{weiss} values of Prussian and Turnbull's blues are more variable when there is much difference in the concentrations of the mixed reactants *e.g.*, $M/5$ with $M/10$; or $M/10$ with $M/5$. This gives further support to the fact, that the composition of such blues is much influenced by the adsorption phenomenon. The Prussian blue is a better adsorbent for Fe^{+++} and $\text{Fe}(\text{CN})_6^{+++}$ than is Turnbull's blue for Fe^{++} and $\text{Fe}(\text{CN})_6^{++}$; hence, we observe that the P_{weiss} values of Prussian blue are farther away from the theoretical value (16.5) than those of the Turnbull's blues. Hence, in Table III the variations of P_{weiss} values can only be accounted for by the different degrees of adsorption of the iron, ferro- and ferricyanogen ions, when the blues are precipitated by mixing the respective reactants in unequal concentrations. Thus, when mixed in equivalent proportion, the ferric ion should be adsorbed more than the ferrocyanogen ion, when the ferric chloride is stronger in concentration than potassium ferrocyanide and *vice versa*. Hence, the P_{weiss} values of these blues would slightly increase or decrease according to the P_{weiss} value of the ion adsorbed.

This view has been practically supported in most cases by the results recorded in Tables III and IV. Magnetic susceptibilities of these compounds, therefore, fairly support the conclusions of the author's analytical results, and the conclusions arrived at from the absorption spectra of their solutions (*J. Indian Chem. Soc.*, 1935, **12**, 143) in oxalic acid are also in agreement with the magnetic behaviour of the fresh and aged samples of these compounds.

My best thanks are due to Prof. P. Rây of Science College, Calcutta, who kindly allowed me to work in his laboratory with the magnetic balance and to Dr. D. C. Sen, now of Ripon College, Calcutta, who kindly helped me in the use of the apparatus.

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Received September 26, 1940.

STUDIES ON OPTICAL ACTIVITY AND CHEMICAL CONSTITUTION. PART V. ROTATORY POWERS OF CAMPHORANILIC ACIDS, α - AND β -NAPHTHYLCAMPHORAMIC ACID AT VARIOUS DEGREES OF NEUTRALISATION.

BY MAHAN SINGH AND ARJAN SINGH.

The rotatory powers of camphoranilic acid, 2', 3', 4'-methylcamphoranilic acids and α - and β -naphthylcamphoramic acids have been determined at various degrees of neutralisation. In every case the alkali salts have greater rotatory power than the acid. In some cases there is a sudden fall at the half neutralisation point and then a progressive increase till the complete neutralisation point. In other cases, after a gradual increase the rotatory powers become constant and then increase till the acid is completely neutralised.

It is well known that the rotations of acids and bases often diminish in magnitude or become reversed in sign when they are converted into their compounds capable of remaining in an ionised state. α -Phenylpropylacetic acid (Pickard and Yates, *J. Chem. Soc.*, 1909, **95**, 101) has a rotatory power $[M]_D = +140.7^\circ$ in benzene but its sodium salt has $[M]_D = +5.0^\circ$ in aqueous solution. The sodium salts of lactic and glyceric acids also suffer a similar reversal of sign.

A change in rotation has also been observed in the cases of 2'- and 4'-dimethylaminocamphoranilic acids (*J. Indian Chem. Soc.*, 1936, **13**, 745). The 2'-dimethylamino acid has a slight positive rotation $[\alpha]_D = 6.2^\circ$ in the neutral medium which increased very little in the presence of alkali, but the rotatory power increased enormously $[\alpha]_D = 57.0^\circ$ when an equivalent amount of an acid was added. 4'-Dimethylaminocamphoranilic acid (*loc. cit.*) likewise shows similar behaviour with acids and alkalis. *p*-Dimethylaminophenylaminocamphor (*J. Indian Chem. Soc.*, 1935, **12**, 219) also resembles these substances in as much as its rotatory power varies considerably when it is converted into its methiodide,

The present paper extends these investigations to the cases of camphoranilic and a few substituted camphoranilic acids as well as to α - and β -naphthylcamphoramic acids both in the pure state as well as in various stages of neutralisation with different alkalis.

Camphoranilic Acid.

The following table contains the rotatory powers of camphoranilic acid at various degrees of neutralisation with LiOH, NaOH and KOH.

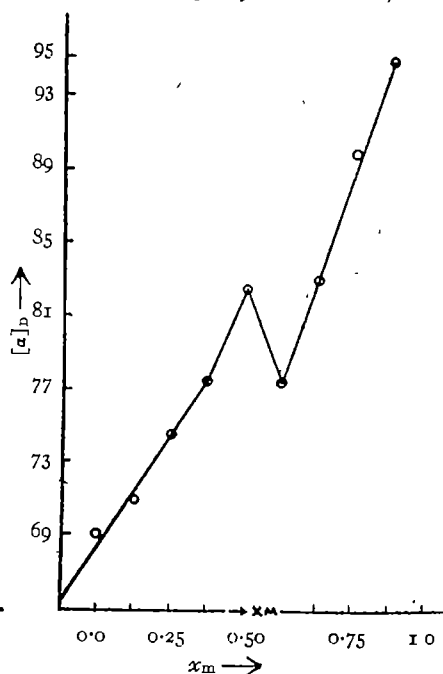
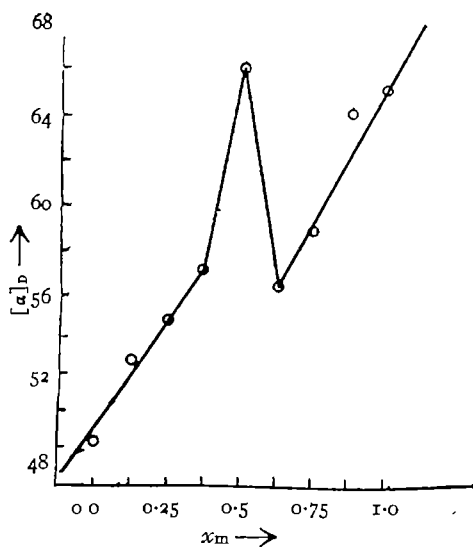
TABLE I.

Solutions of camphoranic acid (0.2750 g./25 c.c.) and increasing amounts of alkali (x_m).

x_m .	[α] _D .			x_m .	[α] _D .		
	LiOH.	NaOH.	KOH.		LiOH.	NaOH.	KOH.
0.00	48.2°	48.2°	48.2°	0.50	69.0°	65.0°	65.4°
0.125	52.7	50.0	51.8	0.625	56.8	59.5	56.8
0.250	54.5	51.8	53.0	0.750	60.0	62.2	60.0
0.375	57.7	54.5	57.8	0.875	66.3	64.5	63.2
				1.00	67.7	67.2	68.2

A series of camphoranic acid solutions were prepared by the addition of the smallest amount of alcohol (2-3 c.c.) and then the required amount of alkali so that solutions with increasing degree of neutralisation were obtained. It will be found that in every case there is a gradual rise till the half neutralisation point. There is then a sudden fall and then a continued rise till the acid is completely neutralised. The result is shown by a typical curve in Fig. 1.

Fig. 1. Camphoranic acid (LiOH).

Fig. 2. β -Naphthylamine (LiOH).

An abrupt change at half neutralisation points to a probability of the formation of a new compound, possibly an acid salt, all attempts at isolation of which have, however, been unsuccessful. It is quite likely that there is a loose combination which breaks up when crystallisation is attempted.

β -Naphthylcamphoranic Acid.

This resembles camphoranic acid very closely in its behaviour. The following table records the values with increasing amounts of LiOH, NaOH, and KOH. In every case there is a steady rise in the rotatory power till the half neutralisation point and then a sudden fall followed by a gradual rise. Here also the values with the exception of that at the half neutralisation point, obey the additive law.

TABLE II.

x_m .	[α] _D .			x_m .	[α] _D .		
	LiOH.	NaOH.	KOH.		LiOH.	NaOH.	KOH
0.00	69.0°	69.0°	69.0°	0.625	77.5°	80.0°	79.5°
0.125	71.0	76.0	72.0	0.750	83.0	83.5	82.0
0.250	74.5	79.0	76.0	0.875	90.0	86.5	85.0
0.375	77.5	81.0	79.5	1.00	95.0	91.0	88.5
0.500	82.5	86.0	84.0				

Changes are all similar and have been typically represented in Fig. 2.

Substituted Camphoranic Acids.

2'-3'- & 4'-Methylcamphoranic acids show a different behaviour from those mentioned above. The following table contains the rotatory powers of these acids with increasing amounts of alkali (x_m).

TABLE III.

2'-Methylcamphoranic acid.						
x_m .	[α] _D .					
	LiOH.			NaOH.		KOH.
0.00	48.0°			48.0°		48.0°
0.125	51.0			50.0		—
0.250	55.0			52.5		58.5
0.375	58.0			55.0		59.0
0.500	57.5			54.5		59.0
0.625	57.5			55.0		59.5
0.750	60.0			57.5		62.0
0.875	63.0			60.5		64.0
1.00	67.0			65.0		66.5

3'-Methylcamphoranic acid.				4'-Methylcamphoranic acid.		
x_m .	[α] _D .			[α] _D .		
	LiOH.	NaOH.	KOH.	LiOH.	NaOH.	KOH
0.00	49.0	49.0	49.0	57.4	57.4	57.4
0.125	50.0	50.0	50.0	59.2	62.3	59.2
0.250	52.5	54.5	52.5	59.2	62.3	59.2
0.375	57.5	58.0	57.5	59.2	63.2	59.6
0.500	57.0	58.0	57.0	59.6	63.6	59.2
0.625	58.0	58.0	58.0	60.1	68.2	63.2
0.750	60.0	—	60.0	64.0	70.0	66.6
0.875	—	62.5	—	68.7	—	70.0
1.00	67.0	68.5	67.0	70.0	76.1	73.5

In all these cases the rotatory powers increase and then become constant till 0.625 of the acid is neutralised, and increase again till the acid is completely neutralised.

α-Naphthylcamphoramic acid behaves like methylcamphoranilic acids. But in this, as already pointed out, the rotatory power of the alkali salts is twice as much as that of the free acid.

TABLE IV.

x_m .	[α] _D			x_m	[α] _D		
	LiOH.	NaOH.	KOH		LiOH.	NaOH.	KOH.
0.00	20.0	20.0	20.0	0.50	31.5	28.5	29.5
0.125	23.5	—	27.0	0.625	31.5	28.0	28.5
0.250	27.0	23.0	—	0.750	36.0	30.5	—
0.375	31.0	27.0	28.5	0.875	39.5	35.5	44.0
				1.00	42.5	40.0	50.5

It is now proposed to study the effect of electrolytes like LiCl, NaCl and KCl etc. on the rotatory powers of the alkali salts and determine some physical constants.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Different Amines.

The method was that described for the condensation of chloroanilines (*J. Chem. Soc.*, 1927, 1995).

The alternative method of heating camphoric anhydride with the amine in chloroform was also used. The chloroform solution is heated for 8-9 hours on the water-bath. Excess of chloroform is removed and the solid mass is crystallised from alcohol.

Camphoranilic acid crystallised from dilute alcohol as a crystalline powder, m.p. 201.5-202.5°. It is soluble in the usual organic solvents.

2'-Methylcamphoranilic acid crystallised into white crystalline mass, m.p. 193.5-94.5.

3'- & 4'-Methylcamphoranilic acid, melt respectively at m.p. 209-209° and 212.5-214.5°.

α-Naphthylcamphoramic acid, m.p. 231.5-232.5° and *β-naphthylcamphoramic acid*, m.p. 212-214° had to be crystallised (animal charcoal) a number of times to free them of the colouring matter.

The rotatory powers of these acids were determined by dissolving a known weight of the acid in 2-3 c.c. of alcohol and then adding a known volume of standard alkali. The remaining volume was made up by adding distilled water.

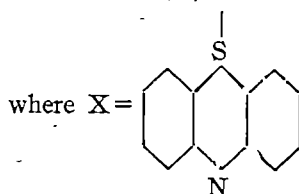
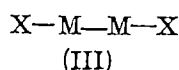
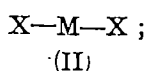


ACRIDINE DERIVATIVES. PART VII. COMPOUNDS WITH MERCURY, COPPER AND ANTIMONY.

By S. J. DAS-GUPTA.

Certain mercury, copper and antimony compounds have been prepared from 5-thiolacridines.

In a previous communication (Das-Gupta, *J. Indian Chem. Soc.*, 1940, 17, 244) some substituted 5-thiolacridines and their gold and silver salts have been described. In the present paper the gold and silver salts of 5-thiolacridine (I, R=H) have been prepared. In addition to this, certain new salts of mercury, copper and antimony have been prepared from the different 5-thiolacridines.



The sodium salt of 5-thiolacridines when treated with mercuric and mercurous salts give compounds of type (II) and (III) (M=Hg) respectively, (the structure of the compounds III being attributed by analogy). The compounds (II) have been isolated in two different forms, yellow and red.

The two varieties of the above mercuric salt have the same melting point and percentage composition suggesting allotropism. Again the sodium salt of substituted 5-thiolacridine gave with a cupric salt, the compounds (II, M=Cu). The sodium salt of 5-thiolacridine, however, gave with copper sulphate a basic compound

The antimony compound of the type (I, R=SbO) has been prepared by treating the sodium salt of 2-chloro-7-methoxy-5-thiolacridine with potassium antimonyl tartrate. This compound is orange-yellow but when heated at 80°-100° becomes red. The red variety has the same melting point as the former, thus suggesting allotropism.

All these compounds are stable but are usually insoluble in common organic solvents. Amongst this group of compounds the aureo as well as the

mercurio compounds seem to be of considerable importance. Their pharmacological properties are being studied.

EXPERIMENTAL.

5-Thiolacridine.—5-Chloroacridine was heated with twice its weight of potassium xanthogenate at 120-30° for 3 hours in phenol solution. The mixture was poured into cold water, the precipitated solids collected, washed with water, and crystallised from rectified spirit in red needles, m.p. 247-49°. (Found: N, 6.51. $C_{13}H_9NS$ requires N, 6.63 per cent).

The compound exists in both ketonic and enolic form. By neutralising a solution of the compound in alcoholic sodium hydroxide, the enolic variety was isolated in yellow needles (m.p. 247-49°) which changed into the red variety (ketonic) in a short time. By determining the p_H of equimolecular solutions of this compound and 2-chloro-7-methoxy-5-thiolacridine in alcohol, it has been found that the former is less acidic. This observation also indicates that the enolic form of 5-thiolacridine is comparatively less stable.

5-Aurothioacridine was prepared just like the aurothioacridines, previously described (*loc. cit.*). The compound was isolated as a red powder, m.p. 288-90°. (Found: Au, 50.0 $C_{13}H_8NSAu$ requires Au, 48.4 per cent).

5-Argentothioacridine.—5-Thiolacridine was dissolved in alcohol and equivalent amount of silver nitrate in aqueous solution was added when a red precipitate was obtained. This was filtered, washed with alcohol and water and dried to a red powder, m.p. 278-80°. (Found: Ag, 34.1. $C_{13}H_8NSAg$ requires Ag, 33.96 per cent).

Mercurio-di-5-thio-(2-chloro-7-methoxy)acridine.—2-Chloro-7-methoxy-5-thiolacridine (0.11 g.) was dissolved in about 10 c.c. of alcohol containing sodium hydroxide (4 c.c. of $N/10$ solution). To this, a solution of mercuric chloride (0.05 g. in 5 c.c. of water) was slowly added and the mixture shaken and left for sometime, when a yellow precipitate settled down. It was filtered, washed with alcohol and water and dried in a steam-oven to a yellow powder, m.p. 284-85°. The compound is soluble in a water-alcohol and other common solvents, yield theoretical. [Found: N, 3.82; Hg, 26.2. $(C_{14}H_9ONClS)_2Hg$ requires N, 3.73; Hg, 26.76 per cent].

In the above preparation, if a lesser amount of sodium hydroxide be used, the compound isolated was sometimes red instead of yellow. The red compound also melted at 284° and, mixed melting point with the yellow compound was not depressed. It gave similar results on analysis. [Found: N, 3.6; Hg, 27.31. $(C_{14}H_9ONClS)_2Hg$ requires N, 3.73; Hg, 26.76

per cent]. Evidently the yellow and the red compounds are allotropic modifications. The yellow compound also becomes red when treated with acids, but it is changed to yellow again on treatment with alkali. This red compound is quite different from the former which is not changed by alkali or heating.

Mercurio-di-5-thio- (7-methoxy)-acridine.—7-Methoxy-5-thiolacridine (1 mol.), dissolved in alcohol containing 1 mol. of sodium hydroxide, was mixed with an aqueous mercuric chloride ($\frac{1}{2}$ mol.) solution. After similar treatment as in the previous case, the compound was isolated as yellow powder, m.p. 254° , exhibiting similar properties. [Found: N, 4.23; Hg, 30.0. $(C_{14}H_{10}NS)_2$ Hg requires N, 4.11; Hg, 29.47 per cent].

Mercurio-di-5-thioacridine.—It was prepared from 5-thiolacridine and mercuric chloride in the usual way as a yellow powder, m.p. $298-300^{\circ}$ (decomp.). [Found: Hg, 32.53. $(C_{13}H_8NS_2)_2$ Hg requires Hg, 32.32 per cent].

5-Mercurothio- (2-chloro-7-methoxy)acridine.—2-Chloro-7-methoxy-5-thiolacridine (0.11 g.) was dissolved in absolute alcohol (100 c.c.) containing sodium hydroxide (0.016 g.) and mercurous nitrate (0.12 g. finely powdered) was added and the mixture stirred for several hours when a yellow precipitate was obtained. It was collected, washed with alcohol, and dried to a yellow powder, m.p. $307-8^{\circ}$. [Found: N, 3.27; Hg, 40.85. $(C_{14}H_9ONClS\ Hg)_2$ requires N, 2.95; Hg, 42.22 per cent]. The compound becomes red when treated with dilute acids, but again becomes yellow when heated at about 150° . It is insoluble in common solvents.

5-Mercurothio- (7-methoxy)acridine.—7-Methoxy-5-thiolacridine (1 mol.) was dissolved in absolute alcohol containing sodium hydroxide (1 mol.) and powdered mercurous nitrate (1 mol.) was added. After usual treatment, the compound (yellow) melted at $244-45^{\circ}$. [Found: N, 3.4; Hg, 46.9. $(C_{14}H_{10}ONS\ Hg)_2$ requires N, 3.17; Hg, 45.52 per cent]. It exhibits similar properties.

5-Mercurothioacridine was prepared from 5-thiolacridine and mercurous nitrate in the usual way as a yellow powder, m.p. $293-94^{\circ}$ (decomp.). [Found: Hg, 47.52. $(C_{13}H_8NS\ Hg)_2$ requires Hg, 48.86 per cent].

Cupro-di-5-thio- (2-chloro-7-methoxy)acridine.—2-Chloro-7-methoxy-5-thiolacridine (2 mol.) was dissolved in alcohol containing sodium hydroxide (2 mol.). Aqueous solution (1%) of copper sulphate (1 mol.) was slowly added, and the mixture shaken for some time and left for several hours, when a pinkish brown precipitate was obtained. It was collected, washed with alcohol and water and dried in a steam-oven to a brownish powder, m.p. $291-93^{\circ}$ (decomp.). [Found: N, 3.81; Cu, 9.20.

$(C_{14}H_9ONClS)_2Cu, 4H_2O$ requires N, 4.09; Cu, 9.28 per cent]. The compound contains four molecules of water of crystallisation, which are not removed on heating at 120° but a portion is lost when heated at 150° . The compound is insoluble in water but very sparingly soluble in alcohol, yield theoretical.

Cupro-di-5-thio-(7-methoxy)acridine was prepared from 7-methoxy-5-thiolacridine and copper sulphate solution in the usual way as brownish powder and has been found to possess similar properties, m.p. $313-14^\circ$ (decomp.). [Found: Cu, 10.23. $(C_{14}H_{10}ONS)_2Cu, 4H_2O$ requires Cu, 10.33 per cent].

Cuprio-di-5-thiolacridine (basic).—5-Thiolacridine was dissolved in alcohol containing equivalent amount of caustic soda and treated with copper sulphate solution in the usual way. An almost black compound was isolated, m.p. $284-88^\circ$ (decomp.). The compound seems to be of basic nature. [Found: Cu, 22.0. $(C_{13}H_8NS)_2Cu, CuO$ requires Cu, 22.5 per cent].

Antimonyl-5-thio-(2-chloro-7-methoxy)acridine.—2-Chloro-7-methoxy-5-thiolacridine (1 mol.) was dissolved in alcohol (90%) containing sodium hydroxide (1 mol.). An aqueous solution of sodium antimonyl tartate (1 mol.) was added and the mixture shaken and left for some time, when an orange-yellow precipitate settled, which was filtered, washed with alcohol and water and dried in vacuum to an orange-yellow powder, m.p. 256° . (Found: N, 3.45; Sb, 29.07. $C_{14}H_9O_2NCISSb$ requires N, 3.4; Sb, 29.52 per cent). It becomes deep red when heated in a steam-oven. Melting point of a mixture of the yellow and the red varieties was not depressed. The red variety gave similar results on analysis. (Found: N, 3.39; Sb, 29.2. $C_{14}H_9O_2NCISSb$ requires N, 3.4; Sb, 29.52 per cent).

The yellow and the red varieties are evidently the allotropic modifications of the same compound.

The author expresses his sincere thanks to Dr. U. P. Basu for his kind interest in this investigation.

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Received September 19, 1940.

COMPLEX CHROMI-SELENATES.

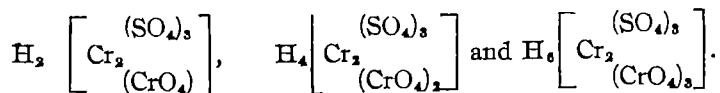
By PRODOSH CHANDRA RAYCHOUDHURY.

Formation of the complexes, chromi-selenic acid, chromi-seleni-chromic acid and romium chromi-seleni-chromate has been studied.

Recoura (*Compt. rend.*, 1892, **114**, 577; 1893, **116**, 1367; 1893, **117**, 37, 131) found that green chromium sulphate combined with aqueous solutions of sulphuric acid and alkaline sulphates in different molecular proportions to form compounds, from which the sulphate ion was not precipitated by barium salts, although the metal introduced with the sulphate could be recognised by means of the usual tests. So these compounds were regarded as salts of a complex acid, chromo-sulphuric acid, $H_2[Cr_2(SO_4)_4]$, resembling hydro-chromi-cyanic acid, $H_2[Cr(CN)_6]$ and chromi-oxalic acid, $H_2[Cr(C_2O_4)_3]$. These chromi-sulphates are not very stable as the sulphate ion in the aqueous solutions is gradually precipitated even in the cold and at once on heating. The chromi-sulphuric acid is stable in the dry air but unstable in aqueous solutions, gradually changing into violet chromium sulphate.

Chromi-di- or tri-sulphuric acids have been obtained by using 2 or 3 molecular proportions of sulphuric acid. They are green powders stable in the solid condition but gradually decompose in solutions. Their constitutions are most probably $H_2[Cr_2(SO_4)_4]$, $H_4[Cr_2(SO_4)_6]$, $H_6[Cr_2(SO_4)_8]$. The corresponding alkaline salts have also been prepared.

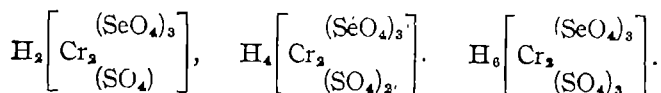
By the combination of chromium sulphate and chromic acid or alkali chromates in molecular proportions, chromo-sulpho-chromic acid and the corresponding alkaline salts have also been prepared [Recoura, *Bull. Soc. Chim.*, 1897, *iii*, **17**, 934]. Like the constitution of the chromo-sulphates the constitutions of these compounds may be



These compounds are unstable. A fresh solution is incapable of yielding precipitates with the Ba or Ag salts but does so after 42 hours.

Sarkar and Bhattacharya (*J. Indian Chem. Soc.*, 1929, **7**, 765) have studied the formation of chromo-seleno-sulphuric acids and their potassium salts. These complexes are prepared by the action of green chromium selenate and selenic acid or sulphuric acid or alkali sulphates in molecular

proportions. Freshly prepared solutions do not give the tests of chromium, sulphate or selenate ions, hence they have the formulae



In the present paper the formation of chromi-selenic acid, chromi-seleni-chromic acids and chromium chromi-seleni-chromate has been studied. These components are generally hygroscopic and soluble in water. The solutions are acidic and freshly prepared solutions do not give any indication of chromic, selenate or chromate ions, except the last compound which gives only the usual test of chromium. So they are all in a complex molecule. These complexes are unstable, the aqueous solutions even at the ordinary temperature decompose after a short time and immediately on heating.

EXPERIMENTAL.

Chromi-selenic Acid.

Green $\text{Cr}_2(\text{SeO}_4)_3, 13\text{H}_2\text{O}$, prepared according to the process described in a previous paper (Raychoudhury, *J. Indian Chem. Soc.*, 1940, 17, 623) was dissolved in water with difficulty and mixed with selenic acid in molecular proportions. The mixture was evaporated to dryness on a water-bath. A green hygroscopic crystalline substance was obtained. It was dried at 120° . The freshly prepared solution did not give any precipitate with ammonium hydroxide or barium nitrate but on boiling precipitates were obtained. {Found : Cr, 15.2 ; Se, 46.1. $\text{H}[\text{Cr}(\text{SeO}_4)_2]$ requires Cr, 15.3 ; Se, 46.6 per cent}.

Tri-selenato-chromic Acid or Acid Chromi-selenate $\text{H}_3[\text{Cr}(\text{SeO}_4)_3]$.

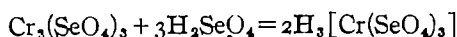
Meyer (*Z. anorg. Chem.*, 1921, 18, 1) obtained the above compound by boiling for a long time the aqueous solution of violet chromium selenate, $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SeO}_4)_3, 3\text{H}_2\text{O}$ and precipitating it as a dark green oil by the addition of a large quantity of alcohol. The green oil when evaporated on the water-bath gave a green compound to which he gave the formula $\text{H}_3\text{Cr}(\text{SeO}_4)_3$.

By boiling solutions of blue $\text{Cr}_2(\text{SeO}_4)_3, 17\text{H}_2\text{O}$ and adding alcohol no precipitate was obtained.

On adding a solution of blue $\text{Cr}_2(\text{SeO}_4)_3, 17\text{H}_2\text{O}$ (Raychoudhury, *loc. cit.*) to a solution of selenic acid in the proportion of one molecule of the former to three molecules of the latter and evaporating the mixture to dryness on the water-bath, a green crystalline mass was obtained. The green solid was :

rubbed with glacial acetic acid, filtered and dried over caustic potash in a vacuum desiccator. {Found: Cr, 10.43; Se, 48.51. $H_3[Cr(SeO_4)_3]$ requires Cr, 10.74; Se, 48.9 per cent}.

The green compound dissolved easily in cold water giving a greenish acidic solution. Freshly prepared cold solution did not give any precipitate with ammonium hydrate or with barium salts. On boiling and adding barium nitrate or ammonium hydroxide, precipitates were obtained. So chromium and selenium must be within the complex molecule. The reaction may be represented thus



Chromi-seleni-chromic Acids.

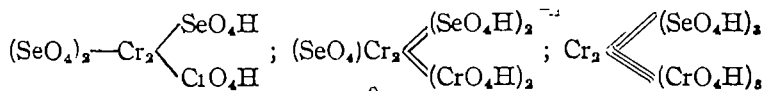
Sarkar and Bhattacharya (*loc. cit.*) prepared chromi-seleni-mono-, di- and tri-sulphuric acids by mixing one, two or three molecular proportions of sulphuric acid with one molecule of green chromi-selenate. Similarly, one molecule of blue $Cr_2(SeO_4)_3, 17H_2O$ was mixed with one, two or three molecules of chromic acid and evaporated in a vacuum desiccator.

(a) *Chromi-seleni-mono-chromic acid* is a brown hygroscopic powder, soluble in water. The yellow solution is acidic. Freshly prepared solutions do not give any precipitate with dilute solutions of silver nitrate, barium nitrate or ammonia. On boiling the complex decomposes. {Found: Cr, 23.85; Se, 36.37. $H_2\left[Cr_2\begin{matrix} (SeO_4)_3 \\ (CrO_4)_2 \end{matrix}\right]$ requires Cr, 23.96; Se, 36.41 per cent}.

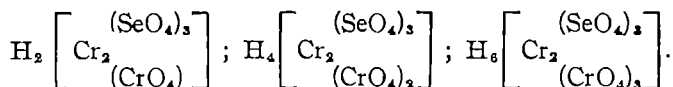
(b) *Chromi-seleni-di-chromic acid* is a reddish brown powder, very hygroscopic and soluble in water. Freshly prepared solution, which is acidic, does not give any test with the above reagents in the cold, but on boiling the tests are obtained. {Found: Cr, 27.12; Se, 31.03. $H_4\left[Cr_2\begin{matrix} (SeO_4)_3 \\ (CrO_4)_2 \end{matrix}\right]$ requires Cr, 27.05; Se, 30.89 per cent}.

(c) *Chromi-seleni-tri-chromic acid* is a chocolate coloured, very hygroscopic powder. It easily dissolves in water making a yellow, acidic solution. Freshly prepared solution does not give any test for chromic, selenate or chromate ions, but on keeping for a short time or on boiling, dilute solutions of silver nitrate, barium nitrate and ammonia give precipitates. {Found: Cr, 30.09; Se, 26.93; $H_6\left[Cr_2\begin{matrix} (SeO_4)_3 \\ (CrO_4)_3 \end{matrix}\right]$ requires Cr, 29.31; Se, 26.61 per cent}.

According to Recoura, (*loc. cit.*) the complexes may have the formulae,



or as suggested by Sarkar and Bhattacharya, (*loc. cit.*)

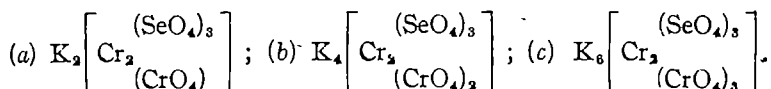


When more than three molecules of chromic acid were mixed with one molecule of blue $\text{Cr}_2(\text{SeO}_4)_3$, $17\text{H}_2\text{O}$ and evaporated on the water bath, a deep chocolate coloured mass was obtained. The mass dissolves readily in water giving a brownish yellow acidic solution which gave a chocolate precipitate of Ag_2CrO_4 with silver nitrate. This proved that the limit of combination had been passed.

Potassium Chromi-seleni-chromates.

By dissolving molecular proportions of the blue $\text{Cr}_2(\text{SeO}_4)_3$, $17\text{H}_2\text{O}$ and potassium chromate in the ratios 1 to 1, 2 or 3 molecules simultaneously in water and evaporating on the water-bath, yellow or brown powders were obtained. They are soluble in water giving yellow solutions which give no precipitate with ammonia, barium nitrate and silver nitrate. On heating, the tests of Cr, SeO_4 and CrO_4 are obtained.

They are the corresponding salts of the above acids, thus



(a) Found : Cr, 21.6 ; Se, 32.7. $\text{K}_2 \left[\text{Cr}_2 \begin{matrix} (\text{SeO}_4)_3 \\ (\text{CrO}_4)_3 \end{matrix} \right]$ requires Cr, 21.47 ; Se, 32.59 per cent.

(b) Found : Cr, 22.7 ; Se, 25.8. $\text{K}_4 \left[\text{Cr}_2 \begin{matrix} (\text{SeO}_4)_3 \\ (\text{CrO}_4)_3 \end{matrix} \right]$ requires Cr, 22.58 ; Se, 25.73 per cent.

(c) Found : Cr, 23.9 ; Se, 21.20. $\text{K}_6 \left[\text{Cr}_2 \begin{matrix} (\text{SeO}_4)_3 \\ (\text{CrO}_4)_3 \end{matrix} \right]$ requires Cr, 23.86 ; Se, 21.26 per cent.

Chromium Chromi-selenato-sulphate.

An aqueous solution of one molecule of green chromium sulphate was evaporated with an aqueous solution of three molecules of green chromium

selenate on a water-bath. A green powder, difficultly soluble in water, was obtained. Excess of ammonium hydroxide gave a precipitate of $\text{Cr}(\text{OH})_3$ in the ice-cold solution; on filtering and boiling the filtrate with excess of ammonia again $\text{Cr}(\text{OH})_3$ was precipitated. So chromium is also in the complex. Dilute solution of barium nitrate gives no precipitate in the freshly prepared cold solution but on boiling a precipitate is obtained, showing that SeO_4 and SO_4 are in the complex. {Found: Cr, 21.10; Se, 36.02; SO_4 , 14.7. $\text{Cr}_2 \left[\text{Cr}_2 \begin{smallmatrix} (\text{SeO}_4)_3 \\ (\text{SO}_4) \end{smallmatrix} \right]_3$ requires Cr, 20.89; Se, 35.71; SO_4 , 14.41 per cent}.

Chromium Chromi-sulphato-selenate.

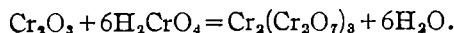
By mixing three molecules of chromium sulphate with one molecule of green chromium selenate and evaporating in the water-bath, a green powder was formed. Excess of ammonia gave a precipitate of $\text{Cr}(\text{OH})_3$ in the freshly prepared ice-cold solution. On filtering and boiling, again $\text{Cr}(\text{OH})_3$ is precipitated proving that chromium is also in the complex. Dilute solutions of barium nitrate gives no precipitate with freshly prepared cold solution, but on boiling a white precipitate is obtained, showing that SeO_4 and SO_4 are in the complex. {Found Cr, 24.52; Se, 13.50; SO_4 , 51.23. $\text{Cr}_2 \left[\text{Cr}_2 \begin{smallmatrix} (\text{SO}_4)_3 \\ (\text{SeO}_4) \end{smallmatrix} \right]_3$ requires Cr, 24.34; Se, 13.87; SO_4 , 50.56 per cent}.

Chromium Chromi-selenato-chromate.

By dissolving equimolecular proportions of chromium chromi-chromate $\text{Cr} \left[\text{Cr} \begin{smallmatrix} (\text{CrO}_4)_3 \\ (\text{H}_2\text{O})_3 \end{smallmatrix} \right]$ and green chromium selenate $\text{Cr}_2(\text{SeO}_4)_3, 13\text{H}_2\text{O}$ simultaneously in water and evaporating in the water-bath, a dark red or chocolate powder was obtained. It is difficultly soluble in water. The freshly prepared cooled solution, when treated with excess of NH_4OH gave a precipitate. After filtration, the filtrate when boiled with excess of ammonia again gives a precipitate of $\text{Cr}(\text{OH})_3$. The freshly prepared solution gives no test for CrO_4 and SeO_4 ions in the cold, but after a very short time (less than half an hour) or immediately if heated, the complex decomposes. {Found Cr^{III} , 20.93; Cr^{VI} , 16.20; Se, 24.3. $\text{Cr}_2 \left[\text{Cr}_2 \begin{smallmatrix} (\text{SeO}_4)_3 \\ (\text{CrO}_4)_3 \end{smallmatrix} \right]_3$ requires Cr^{III} , 21.11; Cr^{VI} , 15.83; Se, 24.06 per cent}.

Chromium Chromi-dichromate.

Calcagni (*Gazzetta*, 1925, 55, 396) by evaporating a solution of Cr_2O_3 in H_2CrO_4 obtained a hygroscopic, amorphous paste, which he named chromium dichromate.



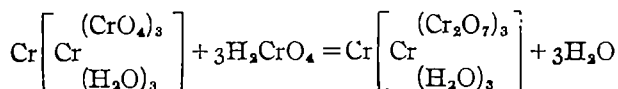
By adopting the above process, no such compound was obtained.

When an aqueous solution of one molecule of chromium chromi-chromate, $\text{Cr} \left[\begin{smallmatrix} (\text{CrO}_4)_3 \\ (\text{H}_2\text{O})_3 \end{smallmatrix} \right]$ was mixed with an aqueous solution containing three molecules of chromic acid and carefully evaporated in the water-bath, deep chocolate coloured shining crystals were obtained. The following table gives a comparative study of the properties of the above compound, chromic acid and chromium chromi-chromate.

TABLE I.

Reagent.	H_2CrO_4 .	New compound.	$\text{Cr} \left[\begin{smallmatrix} (\text{CrO}_4)_3 \\ (\text{H}_2\text{O})_3 \end{smallmatrix} \right]$.
Water.	Readily soluble.	Difficultly soluble (acidic solution).	Difficultly soluble (acidic solution).
$\text{Ba}(\text{NO}_3)_2$.	Yellow ppt.	Brown ppt. after sometime.	Brown ppt. after sometime
$\text{Pb}(\text{Ac})_2$.	Immediate yellow ppt.	Do	Do
NH_4OH	—	Bluish brown ppt.	Bluish brown ppt
AgNO_3 (conc. soln.)	Black ppt.	Voluminous red ppt.	Small quantity of red ppt.
AgNO_3 (very dil. soln.)	Reddish ppt.	No. ppt.	No. ppt.

Since the above compound resembles $\text{Cr} \left[\begin{smallmatrix} (\text{CrO}_4)_3 \\ (\text{H}_2\text{O})_3 \end{smallmatrix} \right]$ more than H_2CrO_4 so the reaction may be regarded as follows :



Found : Cr_2O_3 , 18.5 ; CrO_3 , 75.1 ; Cr_2O_3 , 6 CrO_3 , 3 H_2O requires Cr_2O_3 , 18.86 ; CrO_3 , 74.44 per cent.

My sincere thanks are due to Dr. P. B. Sarkar for suggesting this piece of work.

THE CONDUCTOMETRIC METHOD OF DETERMINING THE SOLUBLE SALT CONTENT OF SOILS FOR USE IN SOIL SURVEY WORK.

BY R. C. HOON, J. K. MALHOTRA, AND LAKSHMI CHAND JAIN.

The conductivity of soil suspensions has been determined with Dionic water tester. The salt content of soils may be derived from the conductivity of 1 : 15 soil suspensions by a very simple relationship, i.e., the conductivity value, if divided by one thousand, gives the percentage salt content of soils.

To determine the total salt content of soils by the present method, the use of distilled water only for making the soil suspensions is suggested as it has been shown that the use of salt-containing water brings about depression in the conductivity value which varies with the nature of the salts present in the water used.

This conductometric method of determining soluble salt content has been tested for a set of soils derived from the various parts of India and the results seem to justify the adoption of this method in this country for soil survey work.

The importance of soil survey work is now well recognised. The classification of soils for project or land reclamation work is mostly based on the p_H values of soils and their soluble salt content. During recent years fairly robust p_H meters have been evolved for field work.

- As early as 1897 Whitney and Mean (*U. S. Dept. Agr. Div. Soil Bull.*, No. 8) suggested the use of a quick electrolytic method for the determination of salt content of soils. The work of Briggs (*U. S. Dept. Agr. Div. Soil Bull.*, 1899, No. 15), Davis and Bryan (*U. S. Dept. Agr. Exp. Sta. Rec.*, 1911, 24, 2107), Davis (*U. S. Dept. Agr.*, 1927, Circ. No. 423) and several others helped considerably to refine the conductometric method. In the present time number of portable types of instruments are available for use by the worker engaged on the survey of soils for purposes of land utilisation or reclamation.

The earlier advocates of the conductometric method determined the electrical conductivity of extracts prepared by centrifuging the soil suspensions. Joseph and Martin (*J. Agric. Sci.*, 1923, 13, 49) measured the specific conductivities of soil extracts at 30° and obtained the percentage salt content by comparing with the specific resistance of a solution containing 1% of sodium chloride and sulphate. Atkins (*ibid.*, 1924, 14, 198) determined the specific conductivities of soil extracts at 0°. More recently, however, Sen and Wright (*ibid.*, 1931, 21, 1), Sen (*ibid.*,

1932, 22, 212) and Dutoit and Perold (*Soil Sci.*, 1935, 39, 59), and others measured the specific conductivities of aqueous suspensions at 25°.

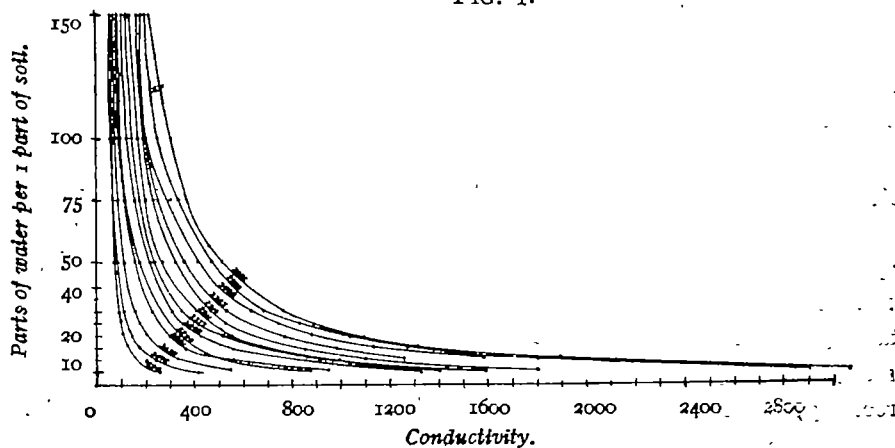
Most of the field workers in conductometric work had used 1:5 soil-water ratio for preparing soil extracts or suspensions. It was considered of interest to determine the conductivity of soil suspensions at different soil-water ratios and to see which ratio afforded values of salt content of soils that agreed most with those obtained gravimetrically.

In the present work measurement of conductivities of soil suspensions was done with Dionic water tester. As the electrode system of this apparatus is graduated for use at temperatures between 10° and 40°, no temperature control was found necessary. The gravimetric determination was done by evaporating an aliquot part of soil extracts prepared from 1:5 soil suspensions.

Effect of Dilution of Soil Suspension on its Conductivity.

The effect of dilution of soil suspension on conductivity was studied for a number of soils at dilutions ranging from 1:5 to 1:150 soil-water ratios. The results are plotted in Fig. 1 and bring out the usual parabolic relationship analogous to that obtained with not very dilute solutions of salts. It was thus indicated that for this type of work it would be better to stick to some one convenient dilution of the soil suspension and to obtain the most suitable relationship for conductivity: soluble salt for that particular soil-water ratio by examining a number of soils of varying salt contents.

FIG. 1.



The Relationship of Salt content of Soils and Conductivity of Soil suspensions at varying Soil-water Ratios.

(a) *1:5 Soil-water Suspensions.*—This concentration of the soil suspension is considered very convenient in soil work. For the gravimetric estimation of the salt content the soil extracts are usually prepared from suspensions of this strength. For the present work the 1:5 soil suspensions were shaken for a few hours and their conductivities were then determined with the Dionic water tester in the usual way. The suspensions were then extracted through porous candles and the salt content of the soil extracts determined gravimetrically. A large number of soils were thus examined. The results of soluble salt content of soils determined gravimetrically (S) and the conductivities of soil suspensions (C) on plotting indicated an almost linear relationship as long as the conductivities did not exceed 400. A statistical examination of the results yielded the following relationship:—

$$10^3 S = 0.314C + 25.4 \quad \dots (i)$$

It is thus clear that for soils having a conductivity of their 1:5 soil suspensions greater than 400, a wider soil-water ratio is to be adopted.

(b) *1:30 & 1:50 Soil-water Suspensions.*—Over 300 soil samples with percentage salt contents varying from 0.1 to 2.0% were taken and the conductivities of their 1:30 and 1:50 soil suspensions determined as before. By computing the salt content of these soils from the conductivities of their 1:30 and 1:50 soil suspensions by formula (i) it was found that the results obtained were comparatively high than the directly determined values. That might be expected as the conductivity dilution relationship is not linear. The conductivities of 1:30 and 1:50 soil suspensions (C) were statistically examined in relation to the directly determined percentage salt content of soils (S) on lines similar to those adopted for obtaining formula (i) and the following two relationships were thus obtained:—

$$\text{For 1:30 soil suspensions: } 10^2 S = 0.17C - 2.8 \quad \dots (ii)$$

$$\text{For 1:50 soil suspensions: } 10^2 S = 0.26C - 0.8 \quad \dots (iii)$$

The results of percentage salt content obtained from the conductivities of soil suspensions at the three dilutions on the basis of the formulae (i)-(iii) for a few soils are given in Table I. A comparison of the results show that the salt contents obtained on the basis of formula (ii) afford a better agreement to the directly determined salt content values than those

TABLE I.

Soluble salt content from conductivity of						Soluble salt content from conductivity of					
No.	Reg. No.	Direct.	1:5 soil suspen- sion by (f).	1:30 soil suspen- sion by (ff).	1:50 soil suspen- sion by (fff).	No.	Reg. No.	Direct.	1:5 soil suspen- sion by (f).	1:30 soil suspen- sion by (ff).	1:50 soil suspen- sion by (fff).
1	3453	0.12%	0.21%	0.16%	0.24%	30	3374	0.42%	0.48%	0.58%	0.43%
2	2903	0.14	0.18	0.18	0.24	31	3338	0.45	0.45	0.55	0.58
3	2894	0.14	0.14	0.18	0.25	32	3004	0.47	0.41	0.41	0.47
4	3002	0.15	0.16	0.18	0.25	33	3468	0.47	0.57	0.48	0.54
5	3009	0.15	0.18	0.18	0.23	34	3330	0.50	0.52	0.55	0.54
6	3204	0.16	0.17	0.15	0.20	35	3302	0.53	0.46	0.57	0.50
7	3205	0.16	0.17	0.22	0.23	36	3287	0.55	0.46	0.52	0.49
8	3017	0.16	0.22	0.23	0.33	37	2985	0.59	0.55	0.59	0.59
9	3196	0.17	0.20	0.26	0.28	38	3019	0.61	0.58	0.57	0.56
10	3088	0.17	0.15	0.19	0.21	39	3465	0.65	0.55	0.57	0.64
11	3366	0.17	0.25	0.24	0.30	40	3321	0.67	0.55	0.62	0.64
12	2889	0.17	0.18	0.21	0.30	41	3445	0.69	0.57	0.64	0.65
13	2893	0.17	0.16	0.21	0.25	42	3189	0.73	0.65	0.72	0.71
14	3007	0.18	0.26	0.23	0.25	43	2988	0.74	0.71	0.71	0.68
15	3072	0.18	0.19	0.18	0.23	44	3137	0.77	0.62	0.70	0.75
16	2978	0.20	0.17	0.17	0.20	45	3027	0.79	0.79	0.74	0.85
17	3090	0.20	0.16	0.18	0.21	46	2916	0.81	0.77	0.81	0.82
18	3176	0.20	0.24	0.31	0.38	47	3262	0.85	0.96	0.86	0.88
19	3370	0.21	0.22	0.24	0.29	48	2975	0.88	0.92	0.89	0.90
20	3229	0.23	0.29	0.30	0.40	49	3280	0.92	0.96	0.92	0.90
21	3333	0.25	0.26	0.28	0.34	50	3304	0.96	0.93	0.89	0.90
22	3174	0.27	0.27	0.30	0.37	51	3323	1.01	0.96	0.98	0.93
23	3257	0.29	0.33	0.31	0.36	52	3325	1.14	1.11	1.15	1.24
24	3329	0.31	0.29	0.31	0.43	53	2993	1.15	1.15	1.10	1.12
25	3233	0.32	0.32	0.31	0.40	54	3157	1.22	1.03	1.16	1.23
26	3378	0.35	0.38	0.48	0.49	55	2973	1.37	1.32	1.25	1.29
27	2999	0.38	0.45	0.40	0.43	56	2972	1.47	1.07	1.50	1.55
28	3463	0.40	0.39	0.32	0.41	57	3058	1.80	1.58	1.59	1.42
29	3309	0.40	0.46	0.47	0.54						

calculated on the basis of the other two formulae when the salt content is of a high order.

(c) 1 : 15 *Soil-water Suspensions*.—During the course of the work it revealed that the conductivities of 1 : 15 soil suspensions divided by one thousand yielded values of total salt content which were almost equal to the values determined gravimetrically, i.e.,

$$S = C \times 1000 \quad \dots (iv)$$

This observation was extremely significant as for 1 : 15 soil suspensions the salt content of soils might be determined from the conductivity values without the use of any complicated formula. To test the point the conductivities of a large number of soils at 1 : 15 dilution of soil suspension were determined. The results of conductivity and total salt content determined gravimetrically are plotted in Fig. 2, from which it is evident that the points lie fairly well along the mean line. The two lines running parallel to the mean line and at a distance equivalent to 0.1% salt content comprise almost all the points up to a salt content of 0.75%. This indicates that up to a conductivity value of 750 the soluble salt content of soils is given by the above relationship subject to a maximum error of 0.1% (the actual error would be less). For soils having conductivity values greater than 750,

$$S = C/1000 + 0.1 \quad \dots (v)$$

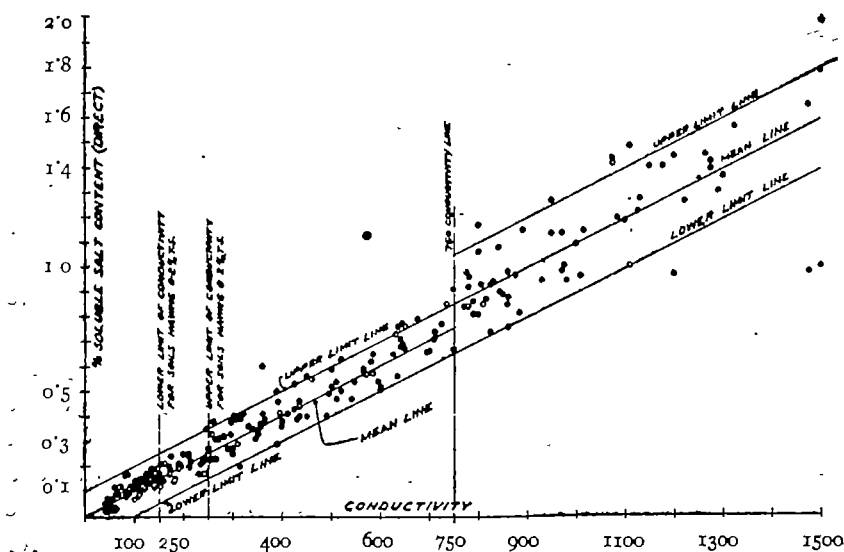
and is subject to a maximum error of 0.2%.

Interpretation of the Results of Soil Analysis for Soil Classification.

For project or land reclamation work the limiting values for soluble salt content and p_H of soils had been fixed as 0.24% and 8.8% respectively for the Punjab soils, i.e. soils having salt content and p_H higher than these values are considered deteriorated and requiring reclamation (Mehta, *Punjab Irrigation Inst. Res. Bull.*, 1927, 39, No. 2). A critical examination was therefore made as to how much error was likely to occur about the limiting value of soluble salt content of soils if the latter was determined conductometrically from 1 : 15 soil suspensions. It was found that for this purpose the limiting values of conductivity could be fixed at 150 and 250 as shown in Fig. 2 by lines AA' and BB', i.e., if the conductivity was less than 150 then the salt content would be less than 0.2% and if the conductivity was more than 250 then the salt content would be greater than 0.2%. For

conductivity values in between the two limits at least 5 results out of 7 would be found to give a correct indication of the salt content.

FIG. 2.



Effect of Shaking of Soil Suspensions.—It is necessary to shake the soil suspensions for 2 to 3 hours before determining the conductivities. This is particularly essential for soils with a high salt content. For soils with low salt content, however, the difference caused by shaking the suspensions in conductivity values is not very significant.

The Quality of Water used for making Soil Suspensions for Conductometric Determination of Total Salt.

Replacement of distilled water for tap or well water obtained locally for making soil suspensions in soil survey work is a significant suggestion. The alternative for distilled water is the tap, well or pump water available at site. The water from any of the latter sources is expected to contain dissolved salts the composition of which will vary from place to place. In order to throw some light on the effect of the salts dissolved in water other than distilled water, a number of samples of water containing NaCl , Na_2SO_4 , Na_2CO_3 , NaHCO_3 and $\text{Ca}(\text{HCO}_3)_2$ in varying proportions were artificially prepared by dissolving the salts in distilled water. The proportion of these salts in different types of waters is given in Table II.

TABLE II.

The proportion of various salts in 100 litres of the artificially prepared waters.

No.	Na_2CO_3 .	NaHCO_3 .	NaCl .	Na_2SO_4 .	$\text{Ca}(\text{HCO}_3)_2$.	Conductivity of water sample.
1	5	10	10	10	15	475
2	—	—	10	10	30	510
3	—	25	10	15	—	550
4	5	15	—	—	30	345
5	—	—	25	25	—	675

It is apparent from the above table that although the total amount of the salts dissolved in the various samples of water is the same still their conductivities are fairly different. The water samples containing NaCl and Na_2SO_4 have the maximum conductivity, while those containing carbonate and bicarbonates have the minimum. The rest have intermediate values of conductivities. Table IV gives the conductivities of the soil suspensions in the above artificially prepared water samples and distilled water—the latter for the sake of comparison. If there is no interaction between the soil and the salts dissolved in water then the following relation should hold good :

$$\begin{array}{ccccc} \text{Conductivity of soil sus-} & = & \text{conductivity of soil} & + & \text{conductivity of the} \\ \text{pension in the salt-} & & \text{suspension in} & & \text{salt-containing} \\ \text{containing water} & & \text{distilled water} & & \text{water.} \\ (A) & & (B) & & (C) \end{array}$$

(A) was, however, invariably found less than the sum of B and C, i.e., a marked depression of conductivity occurred by making the suspension of soil in the salt-containing waters. The depression was found to increase with increase in salt content of soils and varied with different water samples in the following way :—

(i) Minimum depression occurred in water samples containing preponderating amounts of NaCl and Na_2SO_4 .

(ii) Maximum depression occurred in water samples containing more calcium and sodium bicarbonates. In one case, i.e., soil No. 2672 the depression is even more than the conductivity of that soil in distilled water.

(iii) In general the ratio of the conductivity of soil in distilled water to the depression caused by using salt water for making soil suspension instead increases with an increase in the salt content of soils.

From the above it is obvious that the use of waters, other than distilled, produces certain complications on account of the interaction of the salts dissolved in water and the salts associated with soils or the bases in

TABLE III.

Conductivities of soil suspensions in artificially prepared water samples.

Sr. No.	Reg No. of soil	Conductivities of soil suspension in					
		Distilled water.	Artificial water No. 1.*	Artificial water No. 2.*	Artificial water No. 3.*	Artificial water No. 4.*	Artificial water No. 5.*
	Without soil	—	475	510	550	345	675
1	2672	110	500 (85)**	520 (100)**	580 (80)**	340 (115)**	705 (80)**
2	6068	120	500 (95)	560 (70)	550 (120)	400 (65)	740 (55)
3	260	130	540 (65)	560 (80)	600 (80)	360 (115)	750 (55)
4	6066	140	525 (90)	545 (105)	620 (70)	375 (110)	750 (65)
5	2478	140	540 (75)	575 (75)	640 (50)	375 (110)	775 (40)
6	2443	320	690 (105)	750 (80)	560 (310)	350 (315)	925 (70)
7	3019	570	890 (155)	980 (100)	990 (130)	680 (235)	1120 (125)
8	2477	710	1050 (135)	1060 (160)	1120 (140)	880 (175)	1220 (165)
9	2423	830	1200 (105)	1200 (140)	1350 (30)	1050 (125)	1400 (105)
10	3159	850	1200 (125)	1150 (210)	1260 (140)	1010 (185)	1400 (125)

* The composition of the salts dissolved in these waters is given in Table II

** The figures in brackets indicate the depression, *i.e.*, the difference between *B + C* and *A* (*vide supra*).

the exchange complex of soils which affected the conductivities of soil suspensions. Distilled water must therefore be exclusively used for this type of work.

The Use of Conductometric Method of Determining Soluble Salt Content to Soil from Different parts of India

To test this method the soluble salt content of a set of soils obtained from different parts of India was determined conductometrically from their 1 : 15 soil suspensions. The results are given in Table IV and show a fair agreement with the values of soluble salt content determined gravimetrically from soil extracts. It seems, therefore, justifiable that this quick method of determining soluble salt content may usefully be adopted throughout the country for soil survey work.

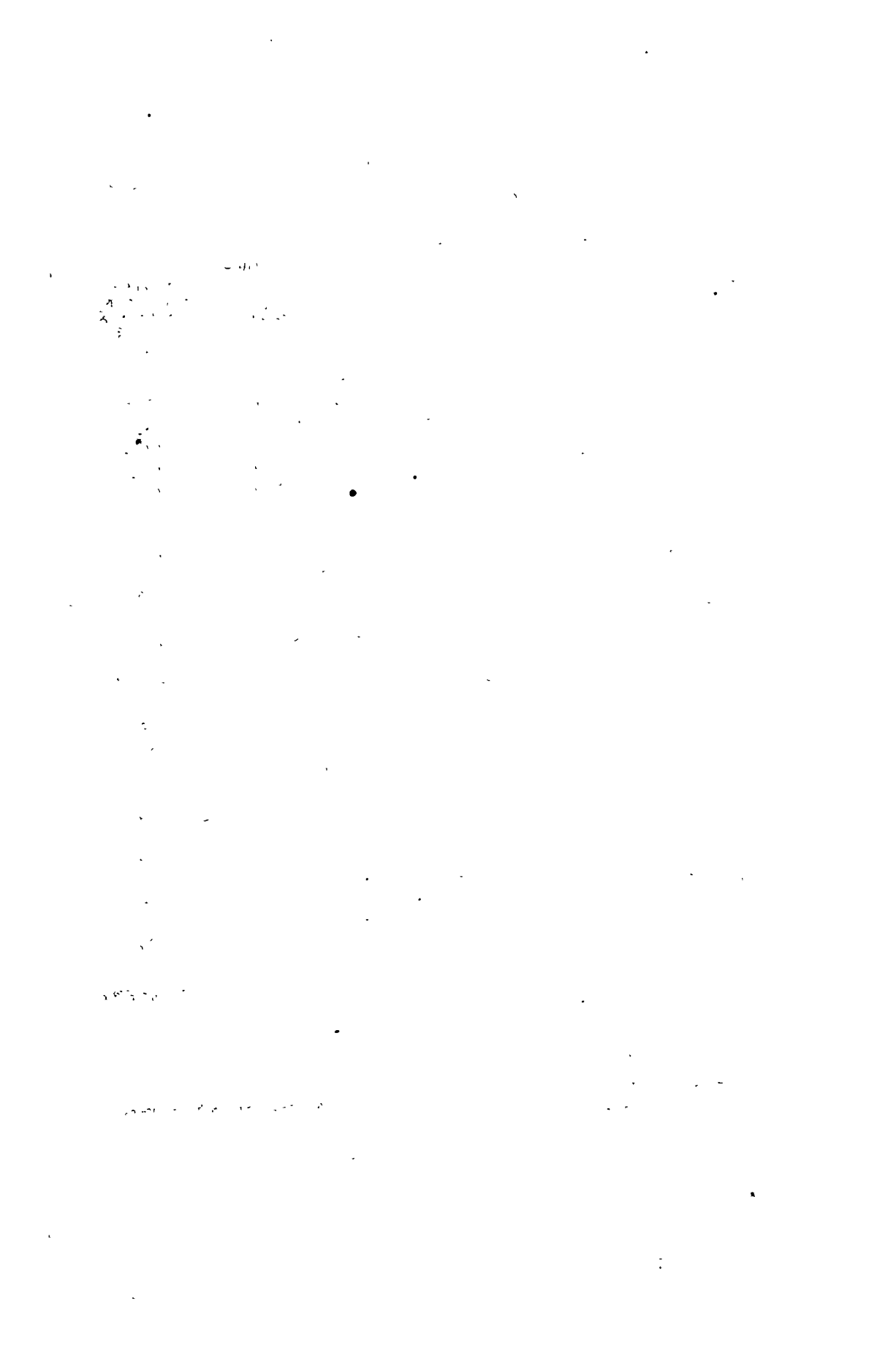
TABLE IV.

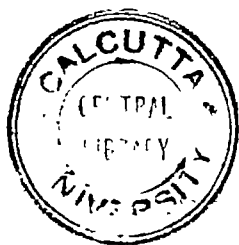
No.	Description of the sample.	Soluble salt content (direct).	Salt content derived from conductivity of 1 : 15 soil suspensions.
1	Surface soil, a composite sample from different estate soils, Coimbatore	0.04%	0.05%
2	Soil sample from Agricultural Farm, Block D surface foot, Tarnab, N.W.F.P.	0.096	0.08
3	Sir Ganga Soil (Punjab).	0.11	0.11
4	Surface soil sample, top 8 inches, Enad Taluk, Malabar....	0.08	0.11
5	Soil sample from Agricultural Farm, Block BP, Tarnab, N.W.F.P.	0.10	0.13
6	Soil sample from Raghupur District, Etawah, U. P. ...	0.09	0.13
7	Surface soil sample from Irrigated cotton field (F. No. 4) Cotton Breeding Station, Coimbatore ...	0.11	0.16
8	Soil sample from plot used for growing kidney beans., Agricultural College Farm, Lyallpur, Punjab. ...	0.18	0.16
9	Bara soil 91/D/4. Punjab.	0.14	0.20
10	Soil sample from Pot Culture House, Shillong. ...	0.21	0.26
11	Soil sample from Toolai Experimental Station, Zorbheta. ...	0.26	0.27
12	Soil sample from Pot Culture House, Kalyanpur. ..	0.296	0.28
13	Soil sample from Pot Culture House, Akola. ..	0.33	0.30
14	Soil sample from Maviya, Khera and Kalli District, Lucknow, U. P.	0.292	0.35
15	Soil sample from treated (1 west) plot, Sakrand, Sind. ...	0.838	1.10
16	Soil sample from untreated plot A/2C2, Sakrand, Sind ...	1.328	1.55
17	Alkali soil sample from Travancore.	1.49	1.70
18	Soil sample from Gursikran (Usar), District Aligarh, U.P..	1.746	1.75
19	Soil sample from Lakhanpur and Kainjari (Usar tract) Tehsil Auraiya District, Etawah, U.P. ...	1.692	1.80

The authors wish to thank Dr. A. N. Puri of this Institute for lending us the set of soil samples.

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Received November 7, 1940.





THE CONDENSATION OF α -SUBSTITUTED ACETO-
ACETATES WITH PHENOLS. PART III. THE
PECHMANN CONDENSATION OF ETHYL
 α -(α -HYDROXY- $\beta\beta\beta$ -TRICHLORO-
ETHYL)-ACETOACETATE

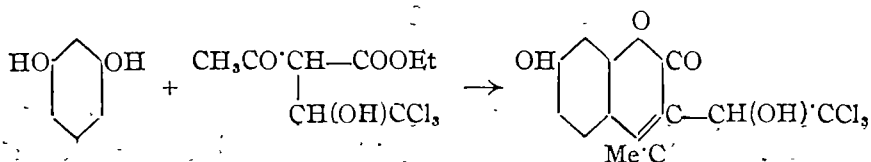
BY D. R. KULKARNI, R. L. ALIMCHANDANI AND N. M. SHAH.

The Pechmann condensation of phenols with ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate has been studied with a view to finding the effect of $-\text{CH}(\text{OH})\text{CCl}_3$ group as an α -substituent on the course of the reaction. Various coumarins containing $-\text{CH}(\text{OH})\text{CCl}_3$ in 3-position and their derivatives have been synthesised.

Much work has been done on the influence of different α -substituents in acetoacetic ester molecule on the course of Pechmann's and Simonis' reactions. The groups mainly studied are (a) simple alkyl groups, and (b) negative substituents like chlorine (*vide* Shah and Shah, *Ber.*, 1938, 71, 2075). In the earlier parts of this series, Shah and Shah (*loc. cit.*) have shown that ethyl α -acetoglutarate condenses with different phenols in presence of sulphuric acid and other condensing agents (Shah, *J. Univ. Bombay*, 1939, 8, 205) to form coumarin-3-propionic acid derivatives; and that ethyl α -acetoglutarate with the α -substituent $-\text{CH}_2\text{CH}_2\text{COOEt}$ containing the carbethoxy group in the chain is more reactive in comparison to simple α -alkyl substituent containing an equal number of atoms.

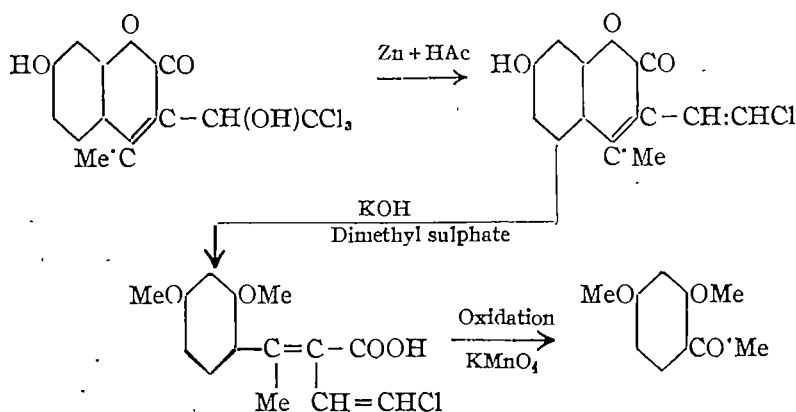
The present investigation was undertaken to study the effect of $-\text{CH}(\text{OH})\text{CCl}_3$ as an α -substituent in acetoacetic ester. In this part are described the results of the condensation of reactive phenols like resorcinol, pyrogallol, α -naphthol, orcinol and phloroglucinol with ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate under the conditions of Pechmann's and Simonis' reactions.

Resorcinol and pyrogallol easily condense in presence of sulphuric acid with the formation of 7-hydroxy- and 7:8-dihydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methylcoumarins respectively; the best yield of the coumarins is obtained by allowing the reaction to proceed for four hours only. The reaction in the case of resorcinol is represented below:



α -Naphthol does not condense in presence of sulphuric acid. This is analogous to the similar behaviour of α -naphthol with α -benzyl acetoacetate (Naik, Desai and Trivedi, *J. Indian Chem. Soc.*, 1929, **6**, 801). Orcinol and phloroglucinol in presence of sulphuric acid give products from which no crystalline substance could be obtained. When sulphuric acid is replaced by phosphorus oxychloride as a condensing agent, the corresponding coumarins are obtained in good yield. In all cases, the condensation in presence of oxychloride proceeds easily at ordinary temperature even without a solvent.

To prove the coumarin structure, the condensation product, derived from resorcinol, has been subjected to hydrolysis and methylation according to the method of Canter and Robertson (*J. Chem. Soc.*, 1931, 1875). Due to the complications arising on account of the hydrolysis of $-\text{CH}(\text{OH})\text{CCl}_3$ group, no definite product is obtained. The condensation product is first reduced by zinc dust and acetic acid (Meldrum and Alimchandani, *J. Indian Chem. Soc.*, 1925, **2**, 1). The Canter-Robertson method fails to convert the reduction product into its *o*-methoxycinnamic acid, which is easily obtained according to the modified method of Shah and Shah (*J. Univ. Bombay*, 1938, **7**, 213); the acid on oxidation gives 2:4-dimethoxyacetophenone, identical with an authentic specimen. The condensation product of pyrogallol has been similarly treated and the corresponding cinnamic acid obtained.



To study the effect of the change of the condensing agent on the above reaction, phosphorus pentoxide (Simonis' reaction) and anhydrous aluminium chloride (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228) have

been tried. Resorcinol and phloroglucinol with phosphorus pentoxide as condensing agent give a poor yield of the respective coumarins identical with the products obtained above. Pyrogallol, α -naphthol and orcinol do not condense at all (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 407). Anhydrous aluminium chloride is found to be unsatisfactory as no product could be isolated. This may be due to the complications arising on account of its side reactions on $\text{CH}(\text{OH})\text{CCl}_3$ group.

EXPERIMENTAL.

7-Hydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methylcoumarin.—To a well cooled mixture of resorcinol (3 g.) and ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate (7.5 g.), sulphuric acid (78%; 30 c.c.) was added in small instalments, the mixture being well shaken after each addition. The colour of the solution gradually changed to deep brown on keeping. After 4 hours, the reaction mixture was poured into crushed ice in thin stream. A yellow semi-solid mass separated; it was repeatedly washed with water and dried. It was first crystallised from acetic acid and then from chloroform as tiny rhombic plates, m.p. $207-8^\circ$ (decomp.), yield 1 g. (Found: Cl, 33.09. $\text{C}_{12}\text{H}_9\text{O}_4\text{Cl}_3$ requires Cl, 32.90 per cent).

The coumarin is easily soluble in alcohol and acetone, difficultly so in chloroform, acetic acid, ethyl acetate and toluene. In alkaline solution, it exhibits blue fluorescence characteristic of a 7-hydroxycoumarin. Alcoholic ferric chloride gives green colour.

The above condensation was studied in presence of (i) phosphorus oxychloride, (ii) phosphorus pentoxide and (iii) aluminium chloride: (i) To a mixture of resorcinol (2 g.) and ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate (5 g.), phosphorus oxychloride (4 c.c.) was slowly added with shaking and cooling; the clear solution was allowed to stand for 12 hours and worked up by adding into water; the solid crystallised from rectified spirit, m.p. $207-8^\circ$ (decomp.) (mixed m.p. with the specimen obtained above), yield nearly 2 g. (iii) The above condensation was repeated with phosphorus pentoxide (10 g.); the mixture was left overnight and after addition of more phosphorus pentoxide (5 g.), was heated on a water-bath for nearly 10 minutes. The oily product obtained was treated with dilute sodium hydroxide, filtered and acidified; the solid obtained on crystallisation from dilute alcohol melted at 206° (mixed m.p. with an authentic coumarin), the yield was poor. (iii) The usual procedure of Sethna, Shah and Shah (*loc. cit.*) was adopted, but no definite product was obtained.

The *acetyl* derivative, prepared with acetic anhydride and a drop of concentrated sulphuric acid, crystallised from rectified spirit as rectangular plates, m.p. 149-50°. (Found: Cl, 25.89. $C_{16}H_{13}O_6Cl$ requires Cl, 26.12 per cent).

The *methyl ether*, prepared by dimethyl sulphate and alkali (2%) in the cold, separated out slowly and was crystallised from dilute alcohol as plates, m.p. 154-55°. (Found: Cl, 30.17. $C_{14}H_{13}O_4Cl$ requires Cl, 30.27 per cent).

The *benzoyl* derivative, obtained by benzoyl chloride and pyridine in cold, crystallised from alcohol as tiny plates, m.p. 169-70°. (Found: Cl, 24.72. $C_{19}H_{13}O_5Cl$ requires Cl, 24.9 per cent). In order to get a dibenzoyl derivative, the benzoylation was tried at a higher temperature; a pasty mass was obtained which could not be crystallised.

7-Hydroxy-3-(β-chlorovinyl)-4-methylcoumarin.—7-Hydroxy-3-(α-hydroxy-βββ-trichloroethyl)-4-methylcoumarin (2 g.) was dissolved in hot glacial acetic acid (30 c.c.). Zinc dust (2 g.) was added in small quantities with stirring. After the reaction was over, the solution was boiled for a few minutes, filtered from unchanged zinc and the filtrate diluted with water, when a solid separated. It was collected and crystallised from dilute alcohol as silky needles, m.p. 254-55° (decomp.). (Found: C, 61.28; H, 3.99; Cl, 14.74. $C_{12}H_9O_3Cl$ requires C, 60.90; H, 3.83; Cl, 14.97 per cent). An alcoholic solution of the substance exhibits blue fluorescence.

The *acetyl* derivative, prepared with acetic anhydride and pyridine, crystallised from rectified spirit, m.p. 169-170°. (Found: Cl, 12.6. $C_{14}H_{11}O_4Cl$ requires Cl, 12.73 per cent).

2:4-Dimethoxy-β-methyl-α-(β-chlorovinyl)-cinnamic Acid.—Dimethyl sulphate (10 c.c.) was first added to a warm solution of the reduction product (1.5 g.) in acetone (20 c.c.). Potassium hydroxide (20%; 50 c.c.) was added and the mixture refluxed on a water-bath for about 1½ hours. Some more dimethyl sulphate and alkali were added at intervals. The mixture was cooled, acidified and extracted with ether. The ethereal extract was treated with sodium bicarbonate solution (5%; 100 c.c.) and the bicarbonate layer acidified; the precipitated acid was crystallised from water in small plates and recrystallised from dilute alcohol, m.p. 172-73°. (Found: Cl, 12.37. $C_{14}H_{13}O_4Cl$ requires Cl, 12.54 per cent).

The *silver* salt was prepared and analysed. (Found: Ag, 27.55. $C_{14}H_{13}O_4ClAg$ requires Ag, 27.7 per cent).

The *cinnamic acid* (1.5 g.) was dissolved in hot acetone (70 c.c.) and aqueous permanganate (2%; 320 c.c.) added in small instalments, the

The *acetyl* derivative, prepared with acetic anhydride and a drop of concentrated sulphuric acid, crystallised from rectified spirit as rectangular plates, m.p. 149-50°. (Found: Cl, 25.89. $C_{16}H_{13}O_6Cl$ requires Cl, 26.12 per cent).

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7-Hydroxy-3-(β-chlorovinyl)-4-methylcoumarin.—7-Hydroxy-3-(α-hydroxy-βββ-trichloroethyl)-4-methylcoumarin (2 g.) was dissolved in hot glacial acetic acid (30 c.c.). Zinc dust (2 g.) was added in small quantities with stirring. After the reaction was over, the solution was boiled for a few minutes, filtered from unchanged zinc and the filtrate diluted with water, when a solid separated. It was collected and crystallised from dilute alcohol as silky needles, m.p. 254-55° (decomp.). (Found: C, 61.28; H, 3.99; Cl, 14.74. $C_{12}H_9O_3Cl$ requires C, 60.90; H, 3.83; Cl, 14.97 per cent). An alcoholic solution of the substance exhibits blue fluorescence.

The *acetyl* derivative, prepared with acetic anhydride and pyridine, crystallised from rectified spirit, m.p. 169-170°. (Found: Cl, 12.6. $C_{14}H_{11}O_4Cl$ requires Cl, 12.73 per cent).

2:4-Dimethoxy-β-methyl-α-(β-chlorovinyl)-cinnamic Acid.—Dimethyl sulphate (10 c.c.) was first added to a warm solution of the reduction product (1.5 g.) in acetone (20 c.c.). Potassium hydroxide (20%; 50 c.c.) was added and the mixture refluxed on a water-bath for about 1½ hours. Some more dimethyl sulphate and alkali were added at intervals. The mixture was cooled, acidified and extracted with ether. The ethereal extract was treated with sodium bicarbonate solution (5%; 100 c.c.) and the bicarbonate layer acidified; the precipitated acid was crystallised from water in small plates and recrystallised from dilute alcohol, m.p. 172-73°. (Found: Cl, 12.37. $C_{14}H_{13}O_4Cl$ requires Cl, 12.54 per cent).

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The *cinnamic acid* (1.5 g.) was dissolved in hot acetone (70 c.c.) and aqueous permanganate (2%; 320 c.c.) added in small instalments, the

2:3:4-Trimethoxy- β -methyl- α -(β -chlorovinyl)-cinnamic Acid.—The reduction product (1.2 g.) in its acetone solution (15 c.c.) was treated with dimethyl sulphate (10 c.c.) and potassium hydroxide solution (20% ; 50 c.c.) on a hot water bath for 1½ hours, as in case of resorcinol. The acid was isolated as before and crystallised from water and recrystallised from a mixture of ether and petroleum ether, m.p. 125-26°. Its silver salt was analysed. (Found: Ag, 25.44. $C_{15}H_{16}O_5ClAg$ requires Ag, 25.74 per cent).

4-Methyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-1:2- α -naphthapyrone.—Phosphorus oxychloride (2 c.c.) was added to a well cooled mixture of α -naphthol (4 g.) and the ester (8 g.) and the mixture left for 40 hours at room temperature. It was then poured into water, the solid well washed with water and crystallised from alcohol and recrystallised from ethyl acetate as needles, m.p. 231-32°, yield 2.5 g. (Found: Cl, 29.84. $C_{16}H_{11}O_3Cl_3$ requires Cl, 29.76 per cent).

The coumarin dissolves sparingly in alkali; in alcoholic solution it exhibits a violet fluorescence; it gives no ferric reaction.

The acetyl derivative, prepared by acetic anhydride and pyridine, crystallised from a mixture of alcohol and acetone as prisms, m.p. 207-8°. (Found: Cl, 26.7. $C_{18}H_{13}O_4Cl_3$ requires Cl, 26.62 per cent).

5-Hydroxy-4:7-dimethyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-coumarin.—To a mixture of orcinol (4 g.) and the ester (9 g.), phosphorus oxychloride (3 c.c.) was gradually added and the mixture left for 40 hours. On working up as before, the substance obtained was crystallised from alcohol, m.p. 223-24° (decomp.), yield 3 g. (Found: Cl, 31.77. $C_{18}H_{11}O_4Cl_3$ requires Cl, 31.51 per cent). The coumarin dissolves in alkali with a non-fluorescent deep yellow colour.

5:7-Dihydroxy-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methylcoumarin.—Phloroglucinol (4 g.) and the ester (9 g.) were treated with phosphorus oxychloride (5 c.c.) and the mixture left for 2 days. It was worked up as in the previous cases. The product crystallised from alcohol and was recrystallised from a mixture of ethyl acetate and petroleum benzene as thin rhombic plates, m.p. 216-17°, yield 3 g. (Found: Cl, 31.12. $C_{18}H_9O_5Cl_3$ requires Cl, 31.33 per cent). The coumarin exhibits violet fluorescence in alcoholic solution and dissolves in alkali with a greenish colour.

This condensation was carried up in presence of phosphorus pentoxide (15 g.) with the reactants in the same proportions as before. Alcohol (3 c.c.) was added as solvent (Chakravarti, *J. Indian Chem. Soc.*, 1931, 8, 410). The mixture was kept for 3 days at room temperature; water was then carefully added and the solution extracted with ether. On removal of

ether, the product was crystallised from alcohol, m.p. 216° (mixed m.p. with the above product). The yield was very poor.

The *acetyl* derivative, prepared with acetic anhydride in pyridine, crystallised from dilute acetic acid and then from a mixture of benzene and petroleum ether, m.p. $147-48^{\circ}$. (Found: Cl, 22.84. $C_{18}H_{18}O_8Cl_3$ requires Cl, 22.86 per cent).

All C-H analyses are micro-determinations by Dr. J. N. Ray, Lahore, to whom our thanks are due.

The authors thank Dr. R. C. Shah for his kind interest in the work.

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Received November 11, 1940

QUINOLINE DERIVATIVES PART VI.

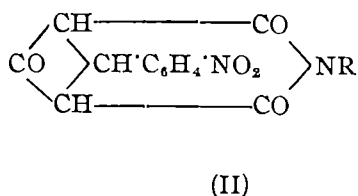
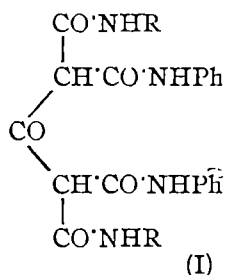
BY DEBABRATA DAS-GUPTA AND TEJENDRA NATH GHOSH.

For obvious pharmacological reasons, a pyridino-quinoline derivative has been synthesised. The condensation product of $\alpha\alpha'$ -phenylcarbamylacetone dicarboxylate and an aromatic amine could not be cyclised to a piperidine derivative.

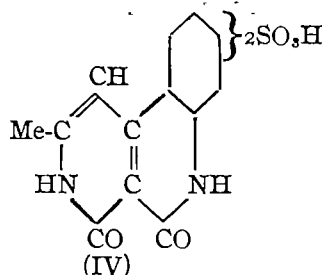
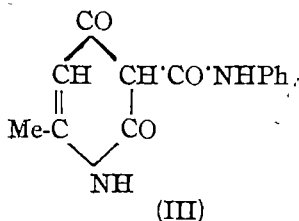
In order to study factors necessary for antiplasmodial action King *et al* (*Proc. Roy. Soc.*, 1938, **B125**, 49, 60) prepared some quinolyl-piperidyl-carbinols, which approach nearly the quinine structure. It was thought of considerable interest to synthesise a compound in which a pyridine ring is fused with the quinoline residue and to see if such a compound possesses any antimalarial properties.

The action of amines on ethyl $\alpha\alpha'$ -phenylcarbamylacetone dicarboxylate (Ghosh and Guha, *J. Indian Chem. Soc.*, 1934, **11**, 355) has now been found to yield the compound (I) and not a piperidine derivative (*cf.* Ruhemann, *J. Chem. Soc.*, 1893, **64**, 259, 874; *Ber.*, 1894, **27**, 1272). All attempts to convert (I) into a piperidine derivative have failed, possibly due to the presence of the keto group.

The NO_2 group in 3:5-*o*-nitrobenzylidene-2:4:6-triketopiperidine derivative (II) (Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 694) could not be reduced by zinc dust and acetic acid to yield a piperidine-quinoline derivative.



2:4-Dihydroxy-3-carbethoxy-6-methylpyridine (Knoevenagel and Fries, *Ber.*, 1898, **31**, 768; 1902, **35**, 2893) has now been allowed to react with aniline at 170° , when the anilide (III) is obtained. When treated with concentrated sulphuric acid, the compound (III) furnishes the sulphonated substance (IV) in which a pyridine ring is fused with the quinoline residue,



EXPERIMENTAL.

αα'-*m*-Tolylcarbamylacetonedicarboxylic Acid Dianilide (I, R = *m*-tolyl).— A mixture of ethyl *αα'*-phenylcarbamylacetone dicarboxylate (4.4 g.) and *m*-toluidine (2.2 g.) was heated in an oil-bath at 160–170° for 4 hours, when alcohol was eliminated. The solid obtained was powdered and washed successively with dilute alkali, dilute hydrochloric acid and water. It was crystallised from glacial acetic acid in yellow rectangular plates, m. p. 206–7°, yield 3 g. (Found: N, 10.12. $C_{33}H_{30}O_5N_4$ requires N, 9.96 per cent).—

Whereas ethyl *αα'*-phenylcarbamylacetone dicarboxylate readily condenses with aldehydes in acetic acid solution (*cf.* Ghosh and Guha, *loc. cit.*; Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 693), the compound (I) does not condense with aldehydes under similar conditions.

αα'-*p*-Tolylcarbamylacetonedicarboxylic acid dianilide (I, R = *p*-tolyl) was prepared in a similar manner. The product crystallised from glacial acetic acid in light orange rectangular plates, m. p. 222–23°. (Found: N, 10.04. $C_{33}H_{30}O_5N_4$ requires N, 9.96 per cent). It is insoluble in dilute alkali and dilute acids.

2:4-Dihydroxy-3-phenylcarbamido-6-methylpyridine (III).— A mixture of 2:4-dihydroxy-3-carbethoxy-6-methylpyridine (9.8 g.) and aniline (4.7 g.) was heated in an oil-bath at 170° for 8 hours. The pasty mass was triturated with acetic acid and the solid was then filtered and washed several times with acetic acid. It was crystallised first from glacial acetic acid and then from benzene in colourless rectangular plates, m. p. 279–80°, yield 4 g. (Found: N, 10.99. $C_{13}H_{12}O_3N_2$ requires N, 11.47 per cent). It gives a reddish colouration with ferric chloride.

2-Hydroxy-6-methylpyridino-3:4 (3'.4')-2-hydroxyquinoline Disulphonic Acid (IV).— The above compound (III, 6 g.) was heated with concentrated sulphuric acid (30 c. c.) in an oil-bath at 100° for 45 minutes. Effervescence was noticed in the reaction mixture, which was allowed to cool and poured into ice-cold water. The mixture was then partially neutralised with sodium bicarbonate. The solid, thus obtained, was crystallised several times from

hot water (charcoal) in colourless crystalline powder, m. p. above 300° , yield 2 g. The compound is strongly acid in reaction and is readily soluble in aqueous sodium bicarbonate solution. That this compound is a sulphonic acid derivative and not a sulphate is proved by the fact that it remains unaffected when treated with aqueous sodium acetate solution. The equivalent weight of this disulphonic acid derivative was determined by titration with standard baryta and the molecular weight was determined. It does not form an oxime and does not give any distinctive colouration with ferric chloride. [Found: C, 39.02; H, 3.74; N, 6.77; S, 15.68, 15.34; H_2O , 4.19; M.W. (by titration), 400. $C_{13}H_{10}O_8N_2S_2 \cdot H_2O$ requires C, 38.61; H, 2.97; N, 6.93; S, 15.84; H_2O , 4.45 per cent.; M.W., 404]. The molecule of water is tenaciously held and is removed completely when the substance is heated at $155-165^{\circ}$ in *vacuo* for about 16 hours. The substance is soluble in cold concentrated hydrochloric acid and is precipitated as a gelatinous mass on dilution with water, which shows that it has got feeble basicity and does not form a stable hydrochloride. Even on boiling with concentrated hydrochloric acid, the hydrochloride could not be obtained. The sodium salt of this compound may, however, prove to be suitable for pharmacological examination. It was contemplated to prepare the acetyl derivative of the compound, from which the corresponding acid chloride and amide could be obtained. The acetyl derivative was, however, obtained as a pasty mass, which could not be crystallised and obtained pure.

The *picrate* was obtained as yellow needles, which began to change to brown at 217° and ultimately became black above 300° .

The authors' thanks are due to Prof. P. C. Guha for his kind interest in this investigation.

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Received September 7, 1940.

THE CONDENSATION OF α -SUBSTITUTED ACETOACETATES
WITH PHENOLS. PART IV. THE CONDENSATION OF
CRESOLS AND OTHER LESS REACTIVE PHENOLS
WITH ETHYL α -(α -HYDROXY- $\beta\beta\beta$ -TRICHLORO-
ETHYL)-ACETOACETATE.

BY D. R. KULKARNI, R. L. ALIMCHANDANI AND N. M. SHAH.

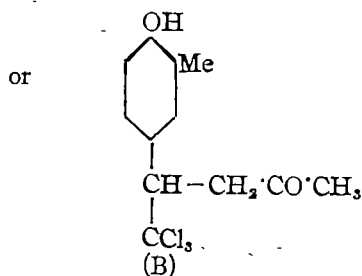
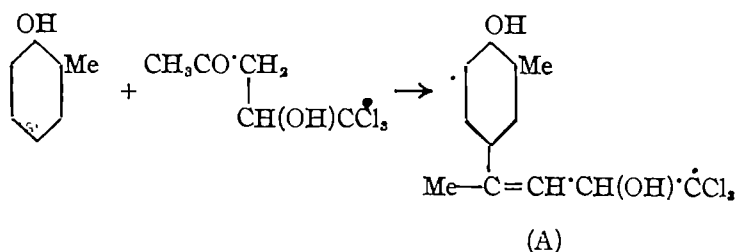
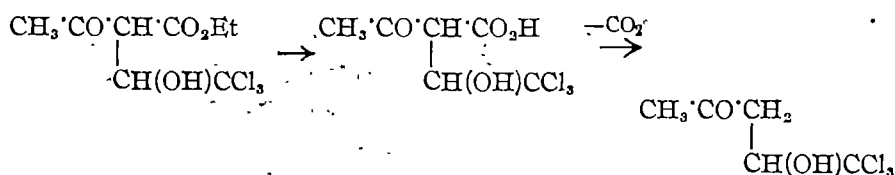
In continuation of Part III, ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate has been condensed with less reactive phenols. The effect of CH (OH) Cl₂ as α -substituent in acetoacetic ester on the course of the reaction has been discussed.

In Part III of this series (*J. Indian Chem. Soc.*, 1941, 18, 113) the authors showed that ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate condensed with different phenols, forming 3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methyl-coumarin derivatives. The above condensation with less reactive phenols like phenol, cresols, β -naphthol, hydroquinone and resacetophenone is described in this part.

Phenol does not give any solid product. Cresols give interesting results. Preliminary experiments indicate that cresols do not undergo the condensation with ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate in presence of sulphuric acid at ordinary temperature. It is, however, observed that *p*-cresol condenses with sulphuric acid as condensing agent at lower temperatures and a satisfactory yield of 4:6-dimethyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-coumarin is obtained by allowing the reaction mixture to remain in a refrigerator for nearly 30 hours. This reaction has also been tried in presence of phosphorus pentoxide to get a chromone, but it does not succeed. Phosphorus oxychloride also proves unsuccessful.

Ortho- and *meta*-cresols, in presence of sulphuric acid alone, give no definite condensation product. The use of alcohol as a solvent facilitates the condensation and a crystalline product could be obtained. An important observation has been made that carbon dioxide is being evolved during the course of the reaction. The purified condensation product from *o*-cresol melts sharply at 186-87°, and the analytical results agree with the formula C₁₅H₁₃O₂Cl₃. It dissolves in alkali and in concentrated sulphuric acid with a yellow colour. Evidently, the pyrone ring is not formed, i.e. the condensation has not taken place in *ortho* position to OH. Assuming that the

reaction takes place in *para* position to OH, as it is more probable, the following scheme represents the course of the reaction :



Of the two alternative structures for the condensation product, the structure (B) is preferred as the product gives (a) a mono-acetyl derivative, and (b) it also gives derivatives characteristic of CO group, *e.g.* semicarbazone.

To get a pyrone derivative, the condensation has been tried under various conditions with phosphorus pentoxide as well as oxychloride, but the reaction does not succeed.

The behaviour of *m*-cresol is exactly similar to that of *o*-cresol described above. This behaviour of *m*-cresol is noteworthy as the *meta*-substituted phenols are generally reactive and give easily coumarins. *m*-Cresol condenses smoothly with ethyl α -acetoglutarate (Shah and Shah, *Ber.*, 1938, **71**, 2075) and acetosuccinate (unpublished) giving the corresponding coumarin-3- acids. Further work on this reaction is being carried out.

The condensation of β -naphthol, quinol and resacetophenone has been tried in presence of sulphuric acid and other condensing agents. No condensation could be effected, either the original phenol being recovered or tarry materials being obtained.

From the results described here and in the previous part, it is clear that the classification of phenols with regard to their reactivity with β -ketonic esters in the Pechmann reaction holds good in case of ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate. Reactive phenols like resorcinol, pyrogallol (*vide* Part III) easily undergo the condensation either in presence of sulphuric acid or phosphorus oxychloride. Phosphorus pentoxide (Simonis' reaction) also gives coumarins though in less yield, whenever the reaction takes place. Less reactive phenols like phenol, β -naphthol etc. do not condense.

The substituent $\text{CH}(\text{OH})\text{CCl}_3$, considered in relation to α -ethyl in ethyl α -ethylacetoacetate, appears to be more reactive judging from the experimental results. The reaction in case of resorcinol and other reactive phenols is completed within a shorter period. *p*-Cresol gives the coumarin only at lower temperature, *o*- and *m*-cresols condense in presence of sulphuric acid, though the reaction takes a different course. No chromone derivative has been obtained in any case with phosphorus pentoxide (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1932, 9, 25). These observations are interesting because the group $\text{CH}(\text{OH})\text{CCl}_3$ is a very heavy substituent compared to ethyl. The increased reactivity of ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate may be attributed to the presence of OH and CCl_3 groups in the alkyl chain.

EXPERIMENTAL.

4:6-Dimethyl-3-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-coumarin.—Cold concentrated sulphuric acid (15 c. c.) was slowly added to the mixture of *p*-cresol (3 g.) and ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate (7.7 g.) cooled by ice. The mixture was then left in the refrigerator for 30 hours. It was then poured into ice and the substance obtained well washed with water. It was digested with acetone and filtered from the tarry matter. On evaporating the solvent, the greenish crystals obtained were recrystallised from toluene as needles, m. p. $202-3^\circ$, yield 1.5 g. (Found: Cl, 33.34. $\text{C}_{13}\text{H}_{11}\text{O}_3\text{Cl}_3$ requires Cl, 33.11 per cent).

The methyl ether, prepared as usual, crystallised from dilute alcohol, m. p. 207° . (Found: Cl, 30.33, 30.0. $\text{C}_{14}\text{H}_{13}\text{O}_3\text{Cl}_3, \text{H}_2\text{O}$ requires Cl, 30.10 per cent).

γ -Trichloromethyl- β -(3-methyl-4-hydroxyphenyl)-propylmethyl ketone.—Cold sulphuric acid (78% ; 15 c. c.) was gradually added to the mixture of *o*-cresol (2 g.) and ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate (5 g.), dissolved in absolute alcohol (12 c. c.) with shaking and cooling. The colour of the solution slowly changed to deep brown on keeping and

carbon dioxide was evolved during the course of the reaction. On the fourth day, the crystals that had separated were collected. The filtrate on further keeping for about 7 days gave a further yield. The product was crystallised from alcohol as feathery crystals, m. p. $186-87^{\circ}$, yield 1 g. (Found: Cl, 36.1. $C_{12}H_{13}O_2Cl_3$ requires Cl, 36.0 per cent). Glacial acetic acid can be used in place of alcohol, but the yield is less in that case.

The *acetyl* derivative, prepared by acetic anhydride and pyridine, crystallised from dilute alcohol in diamond-shaped crystals, m. p. 75° . (Found: Cl, 31.39. $C_{14}H_{15}O_3Cl_3$ requires Cl, 31.52 per cent). The *semicarbazone* crystallised from water as rhombic crystals, m. p. $256-57^{\circ}$. (Found: Cl, 29.95. $C_{13}H_{16}O_2N_3Cl_3$ requires Cl, 30.21 per cent).

γ -Trichloromethyl- β -(2-methyl-4-hydroxyphenyl)-*p*-isopropylmethyl ketone. —*m*-Cresol was condensed exactly in the same manner as *o*-cresol. The product was isolated similarly. Carbon dioxide was evolved. The product on crystallisation from acetic acid and then from methyl alcohol gave rectangular plates, m. p. $208-9^{\circ}$ (decomp.), yield 0.7 g. (Found: Cl, 35.87. $C_{12}H_{13}O_2Cl_3$ requires Cl, 36.0 per cent).

The *acetyl* derivative, prepared as before, crystallised from alcohol in tiny crystals, m. p. $104-5^{\circ}$. (Found: Cl, 31.07. $C_{14}H_{15}O_3Cl_3$ requires Cl, 31.52 per cent).

The *semicarbazone* crystallised from dilute alcohol in needles, m. p. 214° . (Found: Cl, 30.04. $C_{13}H_{16}O_2N_3Cl_3$ requires Cl, 30.21 per cent).

Phenol, β -naphthol, quinol and resacetophenone could not be condensed even with different condensing agents.

Further work is being continued.

The authors thank Dr. R. C. Shah for his interest in the work.

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Received November 11, 1940

PHOTOSENSITISATION BY SOLIDS. PART II*. PHOTOSENSITISED OXIDATION OF AMMONIA IN AQUEOUS SOLUTION WITH TITANIA AS THE PHOTOSENSITISER.

BY G. GOPALARAO AND K. S. MURTY.

The photosensitised oxidation of ammonia in aqueous solution has been studied in the visible light with titania as the photosensitiser. The reaction was found to be zero-molecular. From a study of the influence of concentration of ammonia on the reaction rate and of electrolytes it has been concluded that the reaction is a heterogeneous one occurring at the surface of titania, activated by the absorption of light. The reaction has also been studied in monochromatic light of different wave-lengths. The mechanism of photosensitisation is discussed. The results obtained and the conclusions arrived at lend considerable support to the mechanism proposed by Gopal Rao in the previous part of this series of papers. Experimental results have also been given for the absorption of ammonia by ignited titania.

Photosensitisation by solids is of great practical and theoretical significance. Paints containing titanium dioxide show fading and this phenomenon has been discussed by Kiedel (*Farben Ztg.*, 1929, **34**, 1242), Wagner (*ibid.*, 1929, **34**, 1243; 1929, **35**, 257) and others. The manufacture of panchromatic photographic plates using various dyes as photosensitiser is at present an industry of considerable importance. The process of photosynthesis in the green plants involves photosensitisation by a solid, namely the green pigment chlorophyll. Our knowledge of the mechanism of this photosynthetic reaction is still obscure. The significance to soil chemistry of the results obtained on the photosensitised oxidation of ammonia and the oxidative deamination of amino-acids in light has been emphasised by Gopal Rao and Dhar (*Soil Sci.*, 1931, **31**, 379), Gopal Rao (*ibid.*, 1934, **38**, 143), Gopal Rao and Dhar (*J. Indian Chem. Soc.*, 1934, **11**, 617) and Gopal Rao and Pandalai (*J. Indian Chem. Soc.*, 1934, **11**, 623).

In spite of the great importance of photosensitisation by solids very little attention has been paid to the mechanism of the phenomenon. Recently Gopal Rao (Doctorate Thesis, University of Allahabad, 1934; *Z. physikal. Chem.*, 1939, **184A**, 377) discussed the mechanism of photosensitisation by titania, studying a typical reaction *viz.*, the oxidation of

* Part I of this series appeared in *Z. physikal. Chem.*, 1939, **184A**, 377.

ammonia in ultraviolet light. In the present paper we are giving results of a detailed study of the same reaction in visible light.

EXPERIMENTAL.

The source of visible light was either a 500-watt or a 1000-watt Phillips' tungsten filament lamp. The lamp was connected in series with a thermostat and an ammeter. The 500-watt lamp was worked at 2.2 amperes and the 1000-watt one at 4.4 amperes, on a D.C. circuit. Each lamp was enclosed in a wooden box, painted dull black inside, with a circular aperture in the front. The light issuing out of the aperture was brought to focus by means of a glass condenser. The ammonia solution with the titania was kept in a stoppered quartz cylindrical vessel mounted in a thermostat with quartz windows. The temperature of the thermostat was maintained at $33^{\circ} \pm 0.1^{\circ}$ by constantly circulating water from another thermostat. The ammonia solution was taken out whenever required and the nitrite content estimated colorimetrically by the Greiss-Ilosvay method.

Influence of Concentration of Ammonia.

TABLE I.

40 Ml. of $M/5$ -ammonia + 0.2 g. of ignited titania exposed for 10 hours to light from a 500-watt lamp.

Conc. of ammonia.	Nitrite-N formed per litre of soln.	Conc. of ammonia.	Nitrite-N formed per litre of soln.
$2 \times 10^{-1}N$	2.62 mg.	$2.5 \times 10^{-3}N$	1.36 mg.
1×10^{-1}	2.43	1.25×10^{-3}	1.02
5×10^{-2}	2.33	6.25×10^{-4}	0.76
2.5×10^{-2}	2.22	3.125×10^{-4}	0.64
1×10^{-2}	1.92	1.5625×10^{-4}	0.56
5×10^{-3}	1.61		

From the above results it appears that the photosensitised oxidation of ammonia is a reaction of zero order because the reaction rate is very nearly independent of concentration, *e.g.*, the initial concentration of ammonia can be varied from 0.2 to $0.025N$ (a change of 800%) with a resulting change of only 16% in the rate of reaction, instead of 800% change demanded by a unimolecular reaction.

Influence of the Time of Exposure.

TABLE II.

40 Ml. of M/5-ammonia solution + 0.2 g. of ignited titania exposed to light of a 500-watt lamp.

Nitrite-nitrogen formed per liter of solution.				
Time.	0.2N-NH ₃ .	0.1N-NH ₃ .	0.025N-NH ₃ .	0.0125N-NH ₃ .
5 hrs.	1.30 mg	1.25	1.18	1.02
10	2.59	2.48	2.36	2.01
15	3.93	3.50	3.43	3.04
20	5.30	4.70	4.49	4.12

It can be seen from the above table that the amount of nitrite formed increases proportionately with time and this is in agreement with the idea that the reaction is zero-molecular.

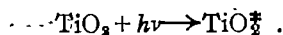
Effect of varying the Amount of the Photosensitiser.

TABLE III.

40 Ml. of M/5- ammonia + titania, exposed to light from a 500-watt lamp for 5 hours.

Titania (g).	0.0031	0.0062	0.0125	0.0250	0.0500	0.1000	0.2000	0.4000	0.8000
Nitrite-N per litre of soln. (mg.)	0.05	0.13	0.27	0.49	0.56	0.94	1.30	1.32	1.35

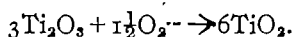
From the above results it is evident that the rate of reaction increases at first proportionately to the increase in the amount of titania and then tends to reach a maximum value with further increase in the amount of titania. It is likely that the photosensitiser titania takes a definite *chemical* part in the reaction. Gopalarao (*loc. cit.*) postulated that the primary reaction is that between the photosensitiser and the ammonia. A molecule of titania gets activated by the absorption of a quantum of light.



The activated titania then oxidises ammonia to nitrite according to the equation,



The titanous oxide then undergoes oxidation to titanium dioxide by molecular oxygen



In order to obtain further support for this theory we kept in a bulb a solution of ammonium carbonate and titanium dioxide. The bulb was sealed after evacuation and then exposed to sunlight. Several such bulbs were exposed. After exposure the bulbs were opened and the solution in each tested for nitrite. Nitrite formation was always noticed. This production of nitrite from ammonia in the absence of oxygen clearly shows that the mechanism of the reaction is of the type postulated above.

Influence of p_{H} on the Reaction Rate.

When a solution of ammonium chloride or ammonium sulphate was exposed to light with titanium dioxide, no nitrite formation was observed. If, however, some calcium or magnesium carbonate was present, nitrite formation readily occurred. Solutions of ammonia or even ammonium carbonate also show nitrite formation when exposed to light in the presence of titania. It appears from this that it is the ammonia and not the ammonium ion that is concerned in the oxidation. It would, therefore, be interesting to study the effect of varying hydrogen ion concentrations on the rate of the reaction. In the following experiments 5 ml. of 1.6N ammonium chloride was added to 35 ml. of a suitable buffer solution of known p_{H} value. It was then exposed to light from a 500-watt lamp, after the addition of 0.2 g. of titanium dioxide. The results obtained are summarised in the following table :

TABLE IV.

p_{H}	Nitrite-N per litre of soln.	p_{H}	Nitrite-N per litre of soln.
7.58	0.44 mg.	9.08	0.92 mg.
8.09	0.48	9.60	0.94
8.61	0.72		

The results show that with increasing p_{H} the rate of nitrite formation increases, though it tends to reach a limiting value.

Influence of various Electrolytes on the Reaction.

It has been suggested by Gopalarao (*loc. cit.*) that the photosensitised oxidation of ammonia is a heterogeneous photocatalytic reaction occurring on the surface of the particles of the photosensitiser. Any factor tending

to reduce the effective surface of the photosensitiser must bring about a decrease in the rate of the reaction. Any substance which can displace the ammonia from the surface of the titania should also have a similar effect. When titania is shaken with ammonia solution it forms a stable suspension which contains particles that carry negative charge. On addition of electrolytes the suspension is coagulated. In this process of coagulation there is agglomeration of the smaller colloid particles into bigger ones, thus reducing the effective surface. Moreover, if polyvalent cations are added they would also displace the adsorbed ammonia. Hence it would be interesting to study the influence of different electrolytes on the rate of the photosensitised oxidation of ammonia.

TABLE V.

20 ml. of $M/2.5$ ammonia + 0.2 g. of titania + electrolyte solution + water to make up to 40 ml., exposed for 3 hours to light from a 1000-watt tungsten filament lamp.

Electrolyte used.	Electrolyte conc.	Nitrite-N per litre of the soln.
Nil	—	1.63 mg.
NaCl	{ 0.01 N	1.40
	{ 0.10	0.92
	{ 0.20	0.95
BaCl ₂	{ 0.005	1.58
	{ 0.010	0.69
	{ 0.100	0.71
AlCl ₃	0.010	0.40

It will be seen from the above results that addition of an electrolyte decreases the amount of nitrite formed. The degree of inhibition produced by a univalent ion like that of Na⁺ is less than that produced by the divalent Ba⁺⁺ ion. It will also be seen from the above table that increasing the concentration of the electrolyte progressively diminishes the rate of oxidation until a steady limiting rate is reached. It is very interesting to note that the limiting reaction rate with divalent ions is somewhat lower than that with univalent ions, while that with trivalent ions is still lower.

From these results we can conclude that the oxidation of ammonia occurs at the surface of titania.

It is well known that hydrated titanous acid tenaciously adsorbs ammonia. According to Weiss and Landicker (*Z. anorg. Chem.*, 1909, **64**, 67) it is very difficult to wash away the last traces of ammonia from precipitated orthotitanous acid. Rose (*Annalen*, 1845, **53**, 267) and Demoly (*Compt. rend. trav. chim.*, 1849, **8**, 325) found that it is very

difficult to free precipitated metatitanic acid from the last traces of ammonia. In order to find out if ignited titanium dioxide used as photosensitiser in our experiments exhibits marked adsorption of ammonia, we have carried out experiments as follows. Merck's pure titanium dioxide was strongly ignited (to 800°), powdered and sieved first through a 60 mesh sieve and finally through a 80 mesh sieve. Ten gram portions of this oxide were shaken up with 200 ml. of a solution of ammonium hydroxide of different concentrations in Jena glass bottles and kept overnight. The supernatant liquid was very turbid and passed freely through a filter paper due to the formation of a colloid. Hence a pinch of pure potassium chloride was added to the solution in each bottle and allowed to settle. The peptised colloidal titania was thus coagulated, leaving the supernatant liquid clear. An aliquot portion of this liquid was taken out with a pipette and titrated with standard sulphuric acid to determine the amount of ammonium hydroxide remaining behind. The difference between this and the amount originally taken gives the amount of ammonia adsorbed. The results are given in the following table.

TABLE VI.

Equib. conc. (m. moles/litre)	0.48	1.26	3.22	7.33	20.0	40.8
Amount adsorbed per g. of TiO_2 (m. moles $\times 10^3$)	6.10	9.23	10.49	13.79	17.90	22.42

From the above results it is clear that considerable adsorption of ammonia occurs at the surface of ignited titania. From Fig. 1, it will be seen that there is a tendency for the surface to be saturated with ammonia even at such a low concentration as 0.04 M.

That adsorption of ammonia on the titania is one of the factors controlling the photosensitised oxidation of ammonia is shown by the similarity of the curves in Figs. 1 and 2. Fig. 1 shows the variation of the adsorbed amount with concentration, while Fig. 2 represents the change of reaction rate with the concentration of ammonia.

FIG. 1.

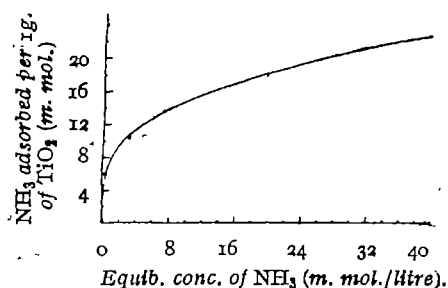
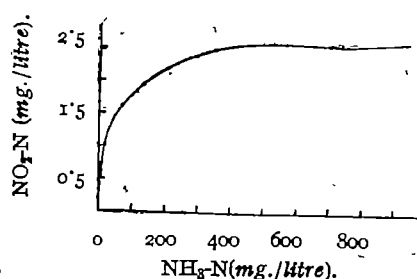


FIG. 2.



*Photosensitised Oxidation of Ammonia with Titania in Monochromatic
Light of different Wave-lengths.*

Aqueous solutions of ammonia are oxidised to nitrite when exposed to ultraviolet light of a quartz mercury vapour lamp but not in visible light. Gopal Rao (*loc. cit.*) has shown that there is a slow oxidation of ammonia in the light of wave-length 3000 Å. According to Landsberg and Predwoditeff (*Z. Physik*, 1925, **31**, 544) the adsorption spectrum of ammonia consists mainly of the bands 1858 Å, 1935 Å, 1990 Å, 2025 Å, 2062 Å, 2144 Å, and also 2195 Å. But in the presence of titanium dioxide the oxidation of ammonia occurs even in the visible region. Results given in the following table show that the oxidation takes place quite rapidly in light of 4050 Å and that there is a slow oxidation even in the light of longer wave-lengths.

TABLE VII.

40 C.c. of ammonia + 0.2 g. of TiO_2 exposed for 20 hours to light from a 1000-watt tungsten filament lamp, through light filters.

Filter.	Transmitted radiation.	Nitrite nitrogen formed per litre in 20-hours.
Yellow : Wallace, M and S, No 5 and No. 7	5300—5850 Å	Traces.
Green, Do. No. 7 and No. 8	5000—5550 Å	0.12 mg.
Blue, Do. No. 8 and No. 3	4450—5000 Å	0.15
Violet : 0.02N-Iodine in carbon tetrachloride (3 cm. layer) + 0.05% quinine hydro- chloride, 1 cm. layer.	4050 Å	4.24

The quinine hydrochloride solution in the last filter undergoes decomposition in the light and is therefore discarded at the end of every hour and replaced by fresh solution. Similar results have been reported by Gopal Rao (*loc. cit.*) working with quartz mercury vapour lamp and filters. Hallet (*Proc. Amer. Soc. Testing Materials*, 1923, **399**; *Chem. Met. Eng.*, 1923, **64**, 29) has shown that titanium dioxide strongly absorbs in the near ultraviolet and ultraviolet parts of the spectrum. Thus titanium dioxide absorbs strongly those wave-lengths which ammonia by itself cannot absorb. Recently Goodeve and Kitchener (*Trans. Faraday Soc.*, 1938, **34**, 570) have stated from study of the reflection spectrum of titania powder that the threshold of absorption lies at about 3800 Å although the position varies slightly according to the method of preparation and treatment of the sample.

DISCUSSION.

The main features of the photosensitised oxidation of ammonia as revealed in this study are:

1. The oxidation of ammonia to nitrite in the presence of titania and sunlight occurs even if air be excluded.

2. Increase in the amount of titania produces an increase in the reaction rate but this soon reaches a limiting value with a constant intensity of light.

3. The amount of nitrite formed increases proportionately with the time of exposure.

4. With constant amount of titania the reaction velocity does not increase in proportion with the increase in concentration of ammonia; only a very slight increase in the reaction rate is produced by a very large increase in the concentration of ammonia.

5. The reaction is retarded by traces of salts of colourless cations like, Na^+ , Ba^{++} , Al^{+++} . The divalent barium ions are more effective retarders than the monovalent sodium ions and the trivalent aluminium ions are more effective than the divalent barium ions.

6. In the presence of titanium dioxide the oxidation of ammonia occurs even in visible light of wave-length 4050\AA and even of higher wave-lengths.

(1) and (2) indicate that the photosensitiser takes part in the reaction. (3) and (4) indicate that the reaction is zero-molecular. This, taken along with (5) shows that adsorption plays an important part in this reaction. The reaction appears to be a heterogeneous catalytic reaction taking place at the surface of titania. A heterogeneous photocatalytic reaction of this kind is somewhat complex and presents a variety of interesting aspects from the theoretical standpoint. When a chemical reaction occurs in a heterogeneous system, there are superimposed upon the specific chemical effects certain interfacial factors, which operate at the boundary of the phases. Dissolved molecules may react with the solid, or undergo catalytic transformation at its surface. The solid may be present as a sediment, or dispersed as a suspension or a colloid. Dissolved molecules must strike and be adsorbed on the surface of the solid before reaction can occur. It has to be realised that the seat of the reaction is the adsorbed layer. And that except in so far as it acts as the reservoir which regulates the concentration of the molecules in this layer, the solution phase is practically outside this reaction. It is the active mass of the substance in the adsorbed layer that determines the rate and order of the reaction. From the Langmuir adsorption isotherm, it is known that the amount of substance adsorbed is

nearly independent of concentration, when adsorption is strong. So also the rate of reaction will be practically constant and independent of concentration. The reaction becomes one of zero order. This has been found to be the case with the photosensitised oxidation of ammonia in the presence of titanium dioxide.

In the case of a heterogeneous photocatalytic reaction there is a further complication. We have to take into account the intensity of the light and the concentration of the light absorbing constituent, *viz.*, the photosensitiser, titania in this case. In Table III it is seen that with increasing amounts of titania, the rate of reaction increases at first proportionately and finally tends to attain a limiting value. This is probably because with the higher amounts of titania the light intensity is becoming the limiting factor. With the smaller amounts of titania, the light intensity from a 500-watt lamp can be assumed to be fairly high; so the amount of light absorbing constituent, titania, determines the rate of the reaction. Hence the rate of reaction increases gradually as the amount of titania increases. But a stage will arrive, when the concentration of titania is no longer limiting the reaction and the intensity of light limits the speed of the reaction. Thus if the intensity of light is kept constant a further increase in the amount of titania does not increase the speed of the reaction. If this hypothesis be correct, an increase in the light intensity at this stage should produce an increase in the reaction rate. In order to put this hypothesis to experimental test, different quantities of titania with the same concentration of ammonia are exposed for 5 hours to light issuing from a 500-watt lamp and also from a 1000-watt lamp. The results are given in the following table.

TABLE VIII.

40 Ml. of *M*/5-ammonia solution exposed with titania for 5 hours.

Titania taken.	Nitrite-N formed per litre	
	with a 500-watt lamp.	with a 1000-watt lamp.
0.8000 g.	1.35 mg.	3.78 mg.
0.4000	1.32	3.41
0.2000	1.30	2.71
0.1000	0.94	—
0.0500	0.56	—
0.0250	0.49	—
0.0125	0.27	—

From the above results it is clear that with a 500-watt lamp the reaction rate reaches a limiting value at about 0.2 g. of titania. With a 1000-watt lamp, the amount of nitrite obtained with 0.2 g. of titania is doubled and increases with increasing amounts of titania.

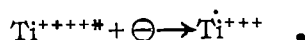
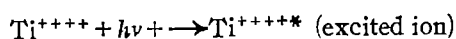
These results are somewhat similar to those of Blackman and Smith (*Proc. Roy. Soc.*, 1911, **83B**, 389) on photosynthesis. It was Blackman who first broke away from the conception of a single optimum factor and developed the theory of interaction of various factors. Blackman and Smith studied the effect of varying concentrations of carbon dioxide on the photosynthetic activity of aquatic plants, *Fontinalis antipyretica* and *Elodea*. They state, "in the weaker solutions of carbon dioxide the curve shows steadily increasing assimilation proportional to the increase of carbon dioxide supply. Here the light intensity and temperature are in excess. But at a certain point, sharply defined increase of carbon dioxide concentration is no longer followed by further increase of assimilation but the value of the assimilation remains at a fixed level.... This part of the curve is due to the limiting action of either illumination or the temperature.... Had a more intense light and a higher temperature been fixed upon, then the ascending part of the curve would have been prolonged further, and a fixed (but higher) level only attained with a greater concentration of carbon dioxide. With less light the limiting value would have been arrived at sooner." In a similar way, Warburg (*Biochem. Z.*, 1919, **100**, 230) working on the photosynthetic activity of unicellular green algae, *chlorella*, found that at low concentrations of carbon dioxide, the rate of photosynthesis is closely proportional to the carbon dioxide concentration. Above a concentration about 2×10^{-6} moles per liter, progressive increase in the carbon dioxide concentration results in a continuously smaller increase in the rate of photosynthesis until finally the latter becomes independent of CO_2 concentration. Warburg interprets these results on the basis that the rate of photosynthesis is proportional to the concentration of carbon dioxide, and to the concentration of a second substance which reacts with carbon dioxide. Harder (*Jahrb. Wiss. Bot.*, 1921, **60**, 531) from an extensive study, stated that certain modifications are necessary, in the simple principle of limiting factors, proposed by Blackman and Smith (*loc. cit.*).

From what has been said above, it appears that the photosynthetic reaction in the green plant is a heterogeneous photosensitised reaction, where possibly the photosensitiser (like the titania in our reaction) takes an active part in the cycle of chemical reactions, though finally regenerated at the at the end of the cycle.

It has been definitely established by our experiments that the photosen-

sitiser, titanium dioxide, takes an active role in the photosensitised oxidation of ammonia. It is likely that a Ti^{++++} ion in a molecule of TiO_2 on the surface gets electronically excited on the absorption of quantum of light. An electron is raised to a higher energy level and according to Franck and Haber (*Sitzber. Preuss. Akad. Wiss.* 1931, 250) such a molecule, atom or ion which possesses an unoccupied electronic level can take up an electron from a reducing substance which functions as an electron donor.

Thus



The photoactive particle takes up an electron and hence gets reduced. The reducing substance which donates the electron gets oxidised.

This mechanism of photosensitisation by titania receives support from the observation of Goodeve and Kitchener (*Trans. Faraday Soc.*, 1938, 34, 902) that the threshold of absorption for solid titania lies in the same region of the spectrum as that of the ions in solution. This may be taken to indicate that the absorption of light by this substance is due to the titanium ions and these are raised to an excited level.

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Received November 11, 1940.

The experimental work reported here formed part of a thesis presented by K.S.M. for the M.Sc. (Hons.) degree of the Andhra University in 1936.

COAGULATION OF COLLOIDS BY EXPOSURE TO HIGH FREQUENCY OSCILLATIONS.

BY SHRIDHAR SARVOTTAM JOSHI AND A. PURUSHOTTAM

Results are given of the exposure of 14 sols to high frequency oscillations from a condensed spark discharge. Coagulation was copious in the majority of cases. The possible effects of intermittent cataphoresis and micellar orientation have been considered. Dielectric absorption and rectification of part of the input A. C. by the micella are suggested as additional factors. •

Spring (*Bull. Acad. Roy. Belg.*, 1900, 483; *Rec. trav. chim.*, 1900, 19, 204) observed that discharges from electrodes *external to the liquid*, point discharges, etc. did not affect the stability of the lyophobic sols. Wilke and Muller (*Kolloid Z.*, 1933, 65, 257) using a more effective arrangement observed that the colour, viscosity, velocity of electrophoresis and electrical conductivity of the arsenious sulphide sol altered by applying a high frequency electro-magnetic field. In the course of an investigation in these laboratories, the results of which will be published shortly, on the viscosity of colloids subjected to electric fields due to alternating potentials at low frequencies (Joshi and Subbaiah, *Proc Indian. Sci. Congress, Chem. Sec.*, 1939, III, p. 50.), it was observed incidentally that with special precautions as to the experimental arrangements and an adequate source of energy, the sensitivity of a colloid to a wide range of frequencies of oscillations was appreciable, at any rate, in some of the systems investigated. The following experiments were, therefore, carried out to examine this phenomenon in some detail.

EXPERIMENTAL.

The colloidal solutions in water of a number of materials, listed herein, were prepared by the usual methods. 10 C c. of each of these colloids at different concentrations were taken in an optical cell and exposed to emissions from a heavy condensed discharge of an induction coil of 12-inch spark length. The cell had, at a fixed distance from each other, two aluminium or platinum electrodes, of which one was earthed through an A. C. milliammeter of the rectifier type. The other was connected through a small capacity to an aerial which picked up the high frequency oscillations produced by the discharge of the induction coil. The aerial current flowing through the colloid varied in the range 0.02 to 0.04 milliamp. (r. m. s.),

The time of exposure was kept constant at 5·0 minutes in all the cases. The following results were observed as to the producibility of coagulation amongst the colloids examined.

Sol.	Coagulation.	Sol.	Coagulation.
1. -ve Arsenious sulphide	Copious	8. -ve Manganese dioxide	copious.
2. „ Antimony „	„	9. „ Prussian blue	„
3. „ Sodium oleate (slightly alkaline)	„	10. „ Sulphur	„
4. „ „ „ (more alkaline than No. 3)	„	11. „ Cadmium sulphide	Slight
5. „ Copper ferrocyanide	„	12. „ Mercury „	Nil
6. „ Ferric hydroxide	„	13. „ Vanadic acid	„
7. +ve Ferric hydroxide	„	14. +ve Aluminium hydroxide	„

DISCUSSION.

The well known results on the cataphoresis of colloids suggest that coagulation might occur during the migration *en masse* of the charged micella towards the appropriate electrodes (*cf.* Thomson, *Nature*, 1921, 107, 520; Whytlaw-Gray, Speakman, and Thomson, *ibid.*, p. 619, 620). This, however, requires fields due to continuous potentials. The observations of Muth (*Kolloid Z.*, 1927, 41, 97) with a number of emulsions in water, Blüh on V_2O_5 suspensions (*ibid.*, 1925, 37, 267) show that an orientating influence obtains even under alternating electric fields. The relevant effects in so far as they are analogous to those in electrolysis may, however, be anticipated to be but small at high frequencies.

That the above considerations do not cover the entire picture is indicated by the fact that in our experiments the specific nature of the colloid material is also a factor, since coagulation does not occur in all the systems examined. Results with ferric oxide obtained indicate that the sign of the micellar charge is not a material factor. It is also interesting to see that while, for example, the V_2O_5 suspensions were markedly sensitive to the applied alternating field in respect of micellar orientation (Blüh, *loc cit.*), the corresponding coagulating effect is but negligible (*vide* Table I), under the above conditions. It might be pointed out that experiments were also made with alternating currents of 50 and 500 cycles per second, to which, the colloid, contained in the annular space of a glass ozoniser of the Siemens' type, was subjected for half an hour at about 150 volts (r. m. s.) and by means of a transformer, 6000 to 8000 volts (r. m. s.); there was no sensible coagulation. Prolonged contact of the aluminium and platinum used as

electrodes had, however, no sensitising action. It is suggested that a *dielectric absorption* by the micellar material is possibly an important determinant of the coagulations thus induced. This dielectric absorption is known to be a function of (in fact almost always increases with) the frequency of the oscillations and of the nature of the material exposed. Presumably its influence is similar to that of light (Freundlich and Nathansohn, *Kolloid Z.*, 1921, **28**, 258; Stintzing, *Koll. chem.-Beih.*, 1914, **6**, 132; Schaum, *Wiss. Phot.*, 1913, **12**, 93) and X-rays (Spring, *loc. cit*; Galecki, *Kolloid Z.*, 1912, **10**, 149; Dhar, "Chemical Action of Light," 1931 p. 375-378) under which certain colloids are without effect, while others are sensitised or even stabilised. Similar results were observed by Joshi and co-workers (*J. Indian Chem. Soc.*, 1936, **13**, 217; 1937, **14**, 254) in the "*thermoageing*" of a large number of colloids. It is also likely that depending upon the nature of the micellar substances, a part of the applied potential might be rectified and that the observed coagulation might, in part, be due to this rectified component.

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Received November 4, 1940.

THE INFLUENCE OF VITAMIN-C ON THE INACTIVATION OF ENZYMES BY ULTRAVIOLET LIGHT.

By K. V. GIRI.

Liver phosphatase, sweet potato amylase and pepsin are inactivated when their solutions are exposed to ultraviolet radiation, and vitamin-C is found to protect the enzymes against the inactivation.

It is well known that ultraviolet radiation influences enzyme action. In general, enzymes are inactivated by the radiation. Enzymes and vitamin-C occur together in all the living tissues of plants and animals. It would, therefore, be of interest to know whether vitamin-C has any influence on the destructive action of ultraviolet radiation on enzymes. The present paper describes some preliminary investigation on the influence of vitamin-C on the inactivation of liver phosphatase, sweet potato amylase and pepsin by ultraviolet light.

EXPERIMENTAL.

Liver phosphatase and sweet potato amylase were prepared according to the methods previously described by Giri (*Biochem. J.*, 1939, **33**, 309; *J. Indian Chem. Soc.*, 1934, **11**, 339), and the procedure for the determination of the activity of the phosphatase and amylase was the same as described in previous publications. In the present investigation pepsin (B.D.H.) was used.

The enzyme solutions (phosphatase and amylase) were mixed with either glycine or acetate buffer of known p_H , and equal amounts of the solutions were pipetted into petri dishes (9.2 cm. diam.). To one of the samples known amount of vitamin-C was added, and the solutions were exposed to the unfiltered ultraviolet radiation. Two other samples of the solution, prepared under exactly similar conditions, were kept without exposure to ultraviolet light. The irradiations were made with the help of a quartz mercury vapour lamp (Hanovia, 220 volt D.C.) at a distance of about 19-20 cm. from the arc. To prevent a rise in temperature of the solutions an electric fan was kept running near the lamp. At stated intervals of time aliquots were removed for the estimation of the phosphatase and amylase activities and for the determination of vitamin-C by the usual dye method.

Liver Phosphatase.

Acetone-treated sheep's liver powder (20 g.), prepared according to the method described by Giri (*loc. cit.*), were extracted with 100 c.c. of water for 2 days in presence of toluene and filtered. The clear yellow filtrate was dialysed in collodion bags and centrifuged. After dialysis the extract was used for the experiment.

The experimental solutions were adjusted to p_H 5.0 and 8.5 by the addition of $M/5$ -acetate and $M/10$ -glycine buffer respectively. The compositions of the mixtures were as follows:

$$p_H = 8.5$$

Expt. soln	Enzyme extract	Glycine buffer p_H 8.5	
A.	5 c.c.	5.0 c.c.	2 c.c. vitamin-C (5 mg.)
B.	"	"	2 c.c. water
C.	"	"	2 c.c. vitamin-C (5 mg.)
D.	"	"	2 c.c. water

The solutions A and B were exposed to ultraviolet light for 30 minutes, while the solutions C and D were kept for the same period at 37° in an incubator and the activities determined. The results are presented in Table I A.

$$p_H = 5.0$$

Expt. soln.	Enzyme soln.	$M/5$ -Acetate buffer	
A.	40 c.c.	10 c.c.	10 mg. vitamin C.
B.	"	"	Without vitamin

The experimental solutions A and B were exposed to ultraviolet light and the activities were determined at stated intervals of time.

The composition of the reaction mixture used for the estimation of the phosphatase activity was as follows:

$$\text{Temperature} = 37^\circ \pm 0.1$$

$M/10$ -Glycine buffer (p_H 8.9)	... 20 c.c.	Enzyme extract	10
2% Sodium β -glycerophosphate	... 10	Water	5
0.1 M - $MgCl_2$... 5	Total volume	50

INFLUENCE OF VITAMIN-C ON INACTIVATION OF ENZYMES 143

10 C.c. of the reaction mixture were used for the estimation of inorganic phosphorus by the method of Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375). The results are shown in Table I A.

It appears from Table I that vitamin-C exerts protective action against the destruction of the phosphatase by ultraviolet light. The results in Table I and II show that the vitamin protects the enzyme from inactivation by ultraviolet light at both the acid and alkaline p_H . The loss of vitamin-C during the period of exposure at p_H 5.0 is very little, and the activity of the enzyme is, therefore, completely protected from inactivation at the acid p_H .

TABLE I.

Influence of vitamin-C on the inactivation of liver phosphatase by ultraviolet light.

A. At p_H 8.5. Activity in mg. p. in 10 c.c. of reaction mixture.			B. At p_H 5.0. Activity in mg. p. in 10 c.c. of reaction mixture				
Expt. Soln.	Time of hydrolysis		Exposed for	Expt. soln. A + vitamin C.		Expt. soln. B without vitamin C.	
	2 hrs.	3 hrs.		Duration of hydrolysis.			
				2 hrs.	15 hrs.	2 hrs.	15 hrs.
A. Phosphatase + vitamin-C exposed to ultraviolet light	0.250	0.333	0 min.	0.143	0.730	0.143	0.730
B. Phosphatase ex- posed to ultra- violet light	0.108	0.130	10	0.143	0.730	0.100	0.570
			20	0.133	0.730	0.091	0.533
C. Phosphatase + vitamin-C kept at 37°	0.347	0.444	30	0.133	0.730	0.083	0.421
D. Phosphatase kept at 37°	0.381	0.500	Destruction of vitamin-C in the exptl. soln. A [vitamin-C in the total vol. of the mixture]				
			0 min.	10.0 mg.			
			10	10.0			
			20	9.4			
			30	9.1			

Amylase.

The amylase was prepared from sweet potato according to the method described by Giri (*loc. cit.*). Fresh tubers were minced and dried in the

sun. The sun-dried material was ground to a fine powder. 100 G. of the dry powdered meal were extracted with 400 c.c. of water for about 12 hours in presence of toluene and filtered. The filtrate after dialysis for two days in collodion bags was used for the experiment.

Experimental solutions :

- A. 25 c.c. of *N*/5-acetate buffer (p_H 5.0)
30 c.c. of enzyme extract.
- B. 25 c.c. of *N*/5-acetate buffer (p_H 5.0)
30 c.c. enzyme extract.
10 mg. of vitamin-C.

The solutions were exposed to ultra-violet light in petridishes of 9.0 cm. diameter, at a distance of 19.5 cm. from the arc. The temperature of the solution varied between 16-18°. At known intervals of time 10 c.c. were removed for the determination of the activity of the amylase.

The composition of the reaction mixture was as follows :

- 20 c.c. *M*/5 acetate buffer (p_H 5.6) = 10 c.c.
20 c.c. 2% soluble starch (Merck) soln. = 20
10 c.c. Amylase soln.
Temp. = 37°.

The results are shown in Table II.

TABLE II.

Influence of vitamin-C on the inactivation of sweet potato amylase.

Exposed to ultraviolet,	Amylase activity* after 1 hour's hydrolysis at 37° ± 0.1.		Exposed to ultraviolet.	Amylase activity* after 1 hour's hydrolysis at 37° ± 0.1	
	With vitamin-C.	Without vitamin-C.		With vitamin-C.	Without vitamin-C.
0 min.	165	215	60	165	173
30	165	201	120	161	149

The results show that as in the case of phosphatase, the sweet potato amylase is inactivated when the aqueous solution containing the enzyme is exposed to ultraviolet light. Vitamin-C protects the enzyme from the inactivation. The results also show that vitamin-C inhibits the activity of the amylase. It is found that the activity of the enzyme in presence of vitamin-C is lower than that of the enzyme in its absence. This is in conformity with the findings of Hanes (*Biochem. J.*, 1935, **29**, 2588), who showed that β -amylase, prepared from barley, is inhibited by the vitamin. Although the vitamin exerts inhibiting action on the activity of the amylase, it protects the enzyme from inactivation by ultra-violet light.

* Expressed in mg. of maltose formed in the total volume of the reaction mixture

Pepsin.—0.2% Pepsin (40 c.c.), dissolved in $N/6\text{-HCl}$, was exposed to ultraviolet light in petri dishes of 9 cm. diameter. The distance between the lamp and the solutions was 9 cm. One of the solutions contained 10 mg. of vitamin-C. The activity of the pepsin was determined before and after exposure, by formal titration of the casein solutions treated with the enzyme.

The reaction mixture contained 3% casein adjusted to $pH\ 1.5$. The total volume of the reaction mixture together with the enzyme amounted to 20 c.c. The digestion was carried at 37° for 30 minutes. The results are shown in Table III.

TABLE III. •

Influence of vitamin C on the inactivation of pepsin by ultraviolet light

Exposed for	Activity of pepsin expressed in c.c. of $N/20\text{-NaOH}$.	
	With vitamin-C.	Without vitamin-C.
0 hr.	4.0	4.0
2	3.8	0.4

The results show that vitamin C protects pepsin from inactivation by ultra-violet light.

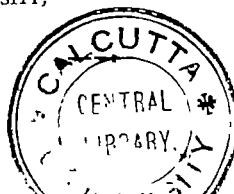
CONCLUSION.

The results clearly indicate that vitamin-C exerts protective action on liver phosphatase, amylase and pepsin against the inactivation by ultraviolet radiation. The protective action on liver phosphatase is exerted at both the acid and alkaline pH . The mechanism underlying the protective action of vitamin-C remains to be elucidated. The discovery of such protective agents like vitamin-C which are distributed in all the tissues of plants and animals would be of great significance, as the presence of such substances would render the ultraviolet light less harmful to enzyme systems, whose activity is kept in tact under the influence of the vitamin.

Part of this work was carried out in the Nutrition Research Laboratories, Coonoor. My thanks are due to Dr. W. R. Aykroyd, Director, Nutrition Research Laboratories, Coonoor, for his interest in this investigation and to Dr. G. Gopal Rao for discussion.

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Received December 26, 1940.



CO-ORDINATED MERCURY COMPOUNDS WITH ETHYLENE AND PROPYLENEDIAMINES.

BY PANCHANAN NEOGI AND KANAI LAL MONDAL

Two different series of complex mercuric salts with propylenediamines have been described, one series is insoluble and the other soluble in water

Though some complex mercuric salts with ethylenediamine are known for sometime, no such compounds with propylenediamine have hitherto been prepared. In this paper, two different series of complex mercuric salts with propylenediamine are described. In one of them mercuric salts combine with the free diamine in equimolecular proportions and form mono-compounds, which are insoluble in water. In the other series, one molecule of a mercuric salt enters into combination with one molecule of a salt of the diamine and forms a complex compound, which dissolves very readily in water. It is to be noted that whilst the solubility of ordinary mercuric salts such as mercuric chloride is of a very limited order, the solubility of the complex mercuric salts of the second series, described here, is very great. These very soluble salts of mercury must possess valuable therapeutic effects the nature and extent of which are being studied. Attempts at preparation of complex mercuric salts with propylenediamine resulted, as in the case of ethylenediamine, in their immediate decomposition with precipitation of grey metallic mercury and the corresponding mercuric salts.

The mono-compounds of the first series dissolve in excess of the diamine and give clear solutions, but compounds of definite composition could be isolated from them. Possibly *bis*-compounds are formed but being very unstable they decompose immediately. Compounds of both the series are more or less stable in air but are easily destroyed by dilute acids and alkalis.

In addition to the complex propylenediamine mercuric salts, several new ethylenediamine compounds of both the series have been described.

EXPERIMENTAL.

Propylenediamine-mercuric Chloride.—Mercuric chloride (1 mol) dissolved in alcohol was added to propylenediamine (1 mol., 70% solution) when a white precipitate of the complex chloride was formed. The same compound was also obtained from an aqueous solution of mercuric chloride.

It is insoluble in water and melts with decomposition above 250° . {Found : N, 8.0 ; Cl, 20.31 ; Hg, 58.35. $[\text{Hg pn}] \text{Cl}_2$ requires N, 8.11 ; Cl, 20.58 ; Hg, 57.97 per cent}.

Propylenediamine-mercuric Bromide.—Mercuric bromide (1 mol.) dissolved in alcohol was added to a molecule of propylenediamine when the complex bromide was precipitated as a white substance. It was washed with water and alcohol and dried in an ordinary desiccator. It melted with decomposition but the melting point was very high. It could not be dissolved in any of the common organic solvents and did not change on keeping. {Found : N, 6.70 ; Br, 37.22 ; Hg, 46.31. $[\text{Hg pn}] \text{Br}_2$ requires N, 6.45 ; Br, 36.87 ; Hg, 46.08 per cent}.

Propylenediamine-mercuric Nitrate.—A saturated solution of mercuric nitrate was prepared and propylenediamine was added to the solution till it ceased to give any white precipitate. The precipitate was washed with water and dried. Excess of water produced hydrolysis and prevented the formation of the complex nitrate. {Found : N, 13.82 ; Hg 50.30. $[\text{Hg pn}] (\text{NO}_3)_2$ requires N, 14.07 ; Hg, 50.25 per cent}.

Propylenediamine Hydrochloride Compound of Mercuric Chloride.—To a saturated solution of mercuric chloride, propylenediamine hydrochloride (1 mol.) dissolved in the least quantity of water was added. The complex chloride was precipitated as white substance. If the solutions used are dilute no precipitate is formed and the mixed solutions have got to be evaporated in vacuum to obtain the complex salt. The precipitate was washed with alcohol several times and then twice crystallised from water. The crystals are very soluble in water and decompose readily with dilute acids including acetic acid. {Found : N, 6.56 ; Cl, 33.5 ; Hg, 47.53. $[\text{Hg pn} \cdot 2\text{HCl}] \text{Cl}_2$ requires N, 6.69 ; Cl, 33.97 ; Hg, 47.84 per cent}.

Propylenediamine Hydrobromide Compound of Mercuric Bromide.—Mercuric bromide was dissolved in alcohol and an equimolecular quantity of propylenediamine hydrobromide, dissolved in the least quantity of water, was added to it. No precipitate was formed. On the addition of a mixture of alcohol and ether, however, a white precipitate of the complex bromide was obtained. It was washed with alcohol thoroughly and then crystallised several times from water in which it was very soluble. {Found : N, 4.48 ; Br, 53.42 ; Hg, 33.21. $[\text{Hg pn} \cdot 2\text{HBr}] \text{Br}_2$ requires N, 4.69 ; Br, 53.67. Hg, 33.55}.

Propylenediamine Hydroiodide Compound of Mercuric Iodide.—To a molecule of an alcoholic solution of mercuric iodide, one molecule of an aqueous solution of propylenediamine hydroiodide was added and the mixture allowed to evaporate in vacuum. A yellowish coloured substance

gradually appeared. It became almost white on crystallising from water. The product was impure. It had to be purified by crystallising several times from water. The complex iodide is even more soluble than the corresponding chloride and bromide and decomposes easily on exposure to air or on keeping for a long time. The colour of the substance then becomes yellow. {Found : N, 3.85 ; I, 64.38 ; Hg, 25.70. $[\text{Hg pn. 2 HI}] \text{I}_2$ requires N, 3.57 ; I, 64.79 ; Hg, 25.51 per cent}.

Propylenediamine Nitrate Compound of Mercuric Nitrate.—To an aqueous solution of mercuric nitrate, an equimolecular proportion of propylenediamine was added. No precipitate was formed. But on the addition of alcohol to the mixture, a precipitate of the complex nitrate gradually appeared. It was perfectly white in colour. {Found : N, 16.39 ; Hg, 37.65. $[\text{Hg pn. 2 HNO}_3] (\text{NO}_3)_2$ requires N, 16.03 ; Hg, 38.17 per cent}.

Ethylenediamine-mercuric nitrate was prepared in the same way as the corresponding propylenediamine compound. {Found : N, 14.77 ; Hg, 51.76. $[\text{Hg pn}] (\text{NO}_3)_2$ requires N, 14.58 ; Hg, 52.08 per cent}.

Ethylenediamine nitrate compound of mercuric nitrate salt was prepared in the same way as the corresponding propylenediamine compound. {Found : N, 16.71 ; Hg, 39.02. $[\text{Hg pn. 2HNO}_3]_2$ requires N, 16.47 ; Hg, 39.21 per cent}.

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Received September 27, 1940

BIGUANIDE SULPHATE AS A REAGENT FOR THE ESTIMATION OF COPPER.

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Copper biguanide sulphate, which forms a very sparingly soluble inner-metallic complex salt of the second order, has been utilised for the estimation of copper. Zinc, cadmium, molybdenum (Mo^{6+}), tungsten (W^{6+}), magnesium and alkali metals do not interfere with the estimation. The solution must not contain any nitrate as the corresponding copper biguanide nitrate is also sparingly soluble. The precipitate, dried at 50° - 70° , has the composition $[\text{Cu}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and is weighed as such. The estimation can be made on both macro and semi-micro scale with very good results, using only a good quality macro analytical balance. In the absence of a large excess of ammonium salt and ammonia the method has also been employed for the volumetric estimation of copper with rubenic acid as an external indicator.

Complex compounds of biguanide and its substitution products with both bivalent and trivalent metals have recently been studied in detail by Rây and co-workers (*J. Indian Chem. Soc.*, 1937, **14**, 670; 1938, **15**, 350, 353; 1939, **16**, 617, 621, 629). They are all inner-metallic complexes of the second order.

The copper biguanide sulphate, which is sparingly soluble at ordinary temperature, is thrown down as a pink coloured, silky precipitate when ammoniacal copper sulphate solution is treated with a solution of biguanide sulphate. The solubility of this complex copper salt at or below 90° is negligible. The precipitate has the composition $[\text{Cu}(\text{BigH})_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, where BigH = one molecule of biguanide. It can be directly weighed after washing first with water, cooled to below 10° , then with alcohol and ether, and finally drying at 50° - 60° . Metals like zinc, cadmium, etc. give no precipitate with biguanide sulphate in ammoniacal solution, and copper can, therefore, be easily separated from these metals by means of this reagent. Molybdenum and tungsten, when present in the form of molybdate and tungstate, do not interfere. Metallic ions, which are precipitated by ammonia, viz., iron, aluminium, chromium, bismuth, antimony, mercury, etc., or form insoluble sulphate, namely, lead, calcium, strontium and barium, obviously interfere with the estimation. Cobalt and nickel, which also give rise to sparingly soluble inner-metallic complex salts with biguanide, must be absent. Anions like nitrate, phosphate, ferrocyanide, arsenate, arsenite, etc., whose copper compounds or copper biguanide

compounds are insoluble or sparingly soluble in ammonia, should also be excluded.

It can also be used for the volumetric estimation of copper by titrating an ammoniacal solution of copper sulphate with a solution of the reagent, the end-point being detected by means of an external indicator like rubeanic acid.

EXPERIMENTAL.

Preparation of Biguanide Sulphate (Reagent).—An intimate mixture of dry dicyandiamide and dry ammonium iodide (1 : 2) was heated on a sand-bath. The molten mass was kept at 173° for five minutes. It was then cooled, extracted with water, rendered ammoniacal and filtered. The filtrate was treated with ammoniacal copper sulphate solution. The precipitated copper biguanide sulphate was filtered, washed and then decomposed with 10% sulphuric acid. On cooling the solution, crystals of biguanide sulphate separated which were recrystallised from water at 60° .

Estimation of Copper as Copper Biguanide Sulphate.

A copper solution was prepared from electrolytic copper and was standardised both electrolytically and by quinaldinate method (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400). To a known volume of the solution, containing no nitrate ion, 0.1 to 0.2 g. of ammonium sulphate was added; it was then treated with ammonia till the solution turned deep blue. The solution was then diluted to 120 c.c., warmed and treated with an excess of biguanide sulphate solution, drop by drop, with constant stirring. A voluminous, wooly, pink-coloured, crystalline precipitate formed at once. The mixture was then cooled in ice to below 10° and allowed to remain at that temperature for about half an hour. It was then filtered through a sintered glass crucible, washed first with cold water (10°) until free from sulphate, afterwards with alcohol and finally with ether. It was dried at 50° - 60° . The dried precipitate has the composition $[\text{Cu}(\text{C}_2\text{N}_3\text{H}_7)_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$ and contains 15.3% copper. Estimations were made on both macro and semi-micro scale. Results are given in Table I, which shows that the amount of copper varying from about 1 mg. to 30 mg. can be determined quite accurately with a good analytical macro balance.

TABLE I.

Wt. of Cu ppt	Cu found.	Cu taken.	Error.	Wt. of Cu ppt	Cu found.	Cu taken.	Error.
0.1809 g.	0.02768 g.	0.02765 g.	+0.00003 g.	0.1410 g.	0.02157 g.	0.02157 g.	...
0.1447	0.02214	0.02212	+0.00002	0.2350 •	0.03595	0.03596	-0.00001
0.1085	0.01660	0.01659	+0.00001	0.2711	0.04148	0.04148	...
0.2170	0.03320	0.03319	+0.00001	0.07175	0.01098	0.01098	...
0.2532	0.03874	0.03872	+0.00002	0.11586	0.01757	0.01757	...
0.2893	0.04426	0.04425	+0.00001	0.1077	0.01648	0.01648	...
0.1989	0.03043	0.03042	+0.00001	0.01085	0.00166	0.00166	...
0.2748	0.04204	0.04204	...	0.00905	0.001384	0.001382	+0.000002
0.2421	0.03704	0.03706	-0.00002	0.0087	0.001327	0.001331	-0.000004
0.1662	0.02543	0.02544	-0.00001	0.007225	0.001104	0.001106	-0.000002

Separation of Copper from Zinc and Cadmium.

The zinc sulphate solution was prepared by dissolving pure zinc in dilute sulphuric acid. The strength of the solution was determined by the quinaldinate method (Rây and Bose, *op. cit.*). The cadmium solution was prepared by dissolving pure $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ in dilute sulphuric acid. The solution was standardised by determining cadmium as sulphate.

The solution containing copper, zinc or cadmium was treated with 1 to 2 g. of ammonium sulphate and then with ammonia till the solution turned deep blue, copper was then precipitated as copper biguanide sulphate as described above. From the filtrate zinc was determined as zinc quinaldinate and cadmium as cadmium sulphate. The results are shown in Tables II and III,

TABLE II.

Wt of Cu ppt.	Wt. of Zn quin- aldinate	Copper		Zinc	
		present.	found.	present.	found.
0'1808 g.	0'1582 g	0'02765 g.	0'02766 g.	0'02420 g.	0'0242 g.
0'2174	0'1742	0'0333	0'0332	0'02662	0'02663
0'1811	0'02765	0'02767
0'07185	0'1742	0'01098	0'01099	0'02662	0'02662
0'0862	0'4745	0'01318	0'01319	0'07260	0'07256
0'11586	0'01757	0'01757
0'0862	0'01318	0'01319
0'1077	0'7908	0'01648	0'01648	0'1210	0'1209

TABLE III.

Cu ppt.	CdSO ₄ .	Copper		Cadmium	
		taken.	found.	taken.	found.
0'2711 g.	0'0971 g.	0'04148 g.	0'04148 g.	0'0573 g.	0'0572 g.
0'2350	0'03596	0'03595
0'1808	0'1951	0'02765	0'02766	0'1147	0'1149
0'2060	0'03153	0'03152
0'2203	0'1365	0'0337	0'0337	0'0803	0'0804
0'2280	0'1166	0'0348	0'0348	0'0688	0'0687

Estimation of Copper in Brass.

A sample of brass (0'3 g. approx.) was dissolved in nitric acid. From the solution, tin and lead, if any, were removed by the usual methods. If any iron and manganese be present, they are removed by ammonia and hydrogen peroxide. Copper was then estimated, as described above, in an aliquot part of the solution. Table IV gives the results obtained.

TABLE IV.

Wt of alloy.	Cu ppt.	Cu found.	Cu present.
2'704 mg.	0'01235 g.	69'87%	70'20%
2'329	0'01070	70'30	70'20
5'160	0'0190	56'35	56'6

Separation of Copper from Molybdenum and Tungsten.

The copper solution containing molybdate or tungstate was treated with an excess of ammonium sulphate (1 to 2 g.) and then with ammonia until a clear blue solution was formed. Copper was then precipitated by adding a large excess of biguanide sulphate in the usual way. Copper biguanide, molybdate and tungstate are soluble in ammoniacal ammonium sulphate solution. Results are shown in Table V.

TABLE V.

Cu ppt.	Cu found.	Cu present.	Substance added (in g.).
0.0960 g.	0.01469 g.	0.01472 g.	0.05 Molybdic acid
0.1147	0.01756	0.01766	0.07 Do
0.0384	0.005875	0.00588	0.07 Do
0.0673	0.00103	0.00103	0.50 Sodium tungstate
0.0479	0.00733	0.00736	0.10 Do

Volumetric Estimation of Copper.

When an ammoniacal solution of copper sulphate is treated with biguanide sulphate solution the simple copper ion is converted into the stable inner complex copper biguanide ion, which does not give the usual tests of the former. This has been utilised for the volumetric estimation of copper with the help of rubeanic acid as an external indicator, the end-point is indicated by the disappearance of the reaction for Cu^{++} ions.

Each copper atom is associated with two molecules of biguanide; therefore a normal solution of copper will be equivalent to a molar solution of biguanide sulphate.

The presence of an excess of ammonium sulphate and ammonia exerts a solvent effect producing $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ in small amount from the complex copper biguanide sulphate, $[\text{Cu}(\text{BigH}^+)_2]\text{SO}_4$. Hence, in the absence of a large excess of ammonium sulphate and ammonia, copper can be satisfactorily titrated with biguanide sulphate at or below 10° . Sharp end-points were obtained even with the very dilute copper solutions. Anions and cations (*op. cit.*), which interfere with the gravimetric estimation, must also be excluded here.

Procedure.—The copper sulphate solution was treated, drop by drop, with ammonia until it turned blue. This was then titrated with biguanide sulphate solution with constant stirring. From time to time a drop of the solution was taken out with a glass rod on a quantitative filter paper and

touched with a drop of dilute rubeanic acid solution in alcohol and the paper dried by holding it over a Bunsen flame. The end-point was indicated by the disappearance of the black spot on the paper. A more accurate result was obtained by making a duplicate titration adding nearly the whole of the calculated volume of biguanide sulphate solution to begin with and then finishing the titration by testing with the external indicator as described. The results are shown in Table VI.

TABLE VI.

Copper soln.	Biguanide sulphate soln.	Copper		Substance added (in g.).
		present.	found.	
100 c.c.	91 c.c.	0.029400 g.	0.02942 g.	...
10	9.1	0.002940	0.002942	...
25	22.75	0.007360	0.007355	...
30	27.35	0.008829	0.008840	...
50	45.66	0.014720	0.01474	...
10	9.3	0.002940	0.002943	0.02 Na tungstate
25	23.3	0.007360	0.00737	0.05 Do
20	18.65	0.005880	0.00590	0.01 Do
10	9.3	0.002940	0.002943	1.0 Zn sulphate
25	23.25	0.007360	0.007359	„ Do
30	27.90	0.008829	0.008830	„ Do

A large excess of ammonium sulphate interferes with the estimation as already stated; this is shown by the results in Table VII

TABLE VII.

Copper soln.	Biguanide sulphate soln	Am. sulphate added.
10 c.c.	9.3 c.c.	0.0 g
10	9.8	2.0
10	10.3	4.0
10	11.4	6.0

In presence of cadmium no sharp end-point could be obtained.

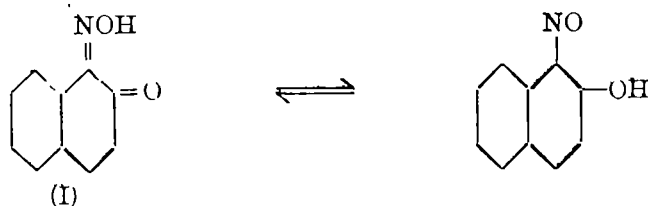
THE USE OF NITROSO DERIVATIVES AS REAGENTS IN INORGANIC ANALYSIS. PART I.

BY S. S. GUHA-SIRCAR AND SASANKA CHANDRA BHATTACHARJEE.

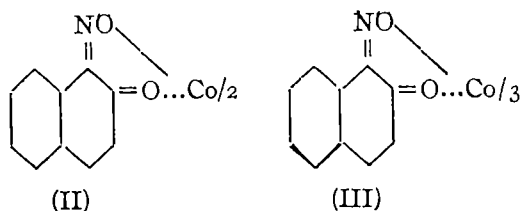
α -Nitroso- β naphthylamine, β -nitroso- α -naphthylamine and Isonitrosodimedone are very satisfactory reagents for the gravimetric estimation of cobalt in the trivalent state. Dinitroso resorcinol and orcinol form bivalent complexes

During recent years many organic reagents acting specifically with particular metallic elements have been discovered and extensively investigated. Some of these furnish very accurate reagents for the quantitative estimation of the metals concerned. Thus all aromatic isonitroso-ketones containing the group $\begin{array}{c} \text{—C=O} \\ | \\ \text{—C=NOH} \end{array}$ e.g. α -nitroso- β -naphthol (I) and β -nitroso-

α -naphthol, form red insoluble inner complex salts with cobalt, the precipi-

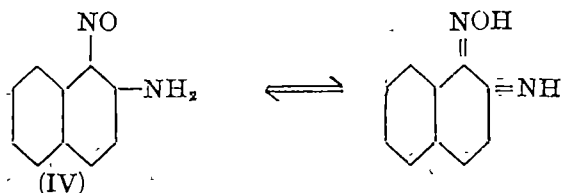


tation being quantitative. But one grave defect of these reagents is that, the precipitate being an arbitrary mixture of divalent complex (II) and trivalent complex (III) is not of pure and definite composition and therefore

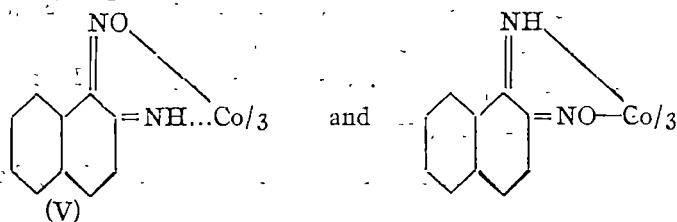


not directly weighable. This defect has been indirectly eliminated by Mayer and Feigl (*Ber.*, 1932, **90**, 15) who previously oxidised the cobaltous solution to the cobaltic state and then precipitated the metal with α -nitroso- β -naphthol. In the present investigation it has been noted that in these reagents, the number of ketonic oxygen atoms has an important influence on the nature

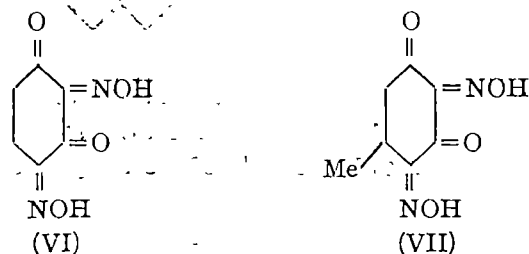
of the complex formed. When present in this reagent, it helps the precipitation of the 'ous' complex and when absent, that of the 'ic' complex. Thus it has been shown in this paper that α -nitroso- β -naphthylamine



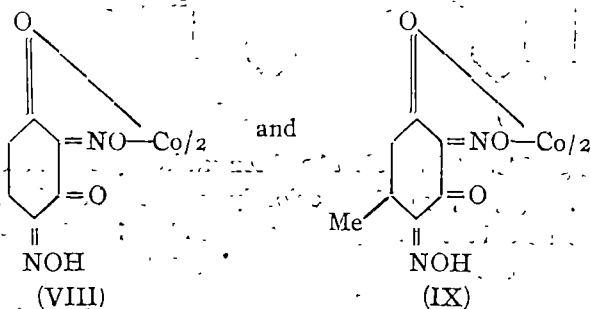
(IV) (Iljenski, *Ber.*, 1884, 17,391) or β -nitroso- α -naphthylamine (Harden; *Annalen*, 1889, 255, 162, 152) which are imino substitution products of the corresponding nitrosonaphthols, produce directly weighable trivalent cobalt complexes (V), no previous oxidation as in the case of Feigl being necessary.



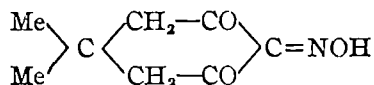
The results of estimation with these reagents are quite accurate. On the other hand, dinitroso-resorcinol (VI) (*J. Amer. Chem. Soc.*, 1923, 45, 1536) and dinitrosoorcinol (VII) (*Ber.*, 1889, 20, 3133) containing two ketonic



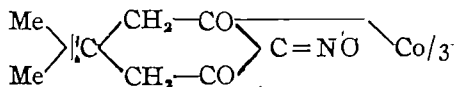
oxygen atoms produce precipitates (VIII and IX) of divalent cobalt.



In the case of isonitroso dimedone,



(*J. Chem. Soc.*, 1907, 1436), though it contains 2 ketonic oxygen atoms, it produces a directly weighable cobaltic complex



indicating that for the formation of cobaltous complex the presence of benzenoid character, as in the dinitrosoresorcinol, is essential. Here also no previous oxidation is necessary. The precipitates in this case are not so stable as in the other cases.

EXPERIMENTAL.

α-Nitroso-β-naphthylamine (Iljenski, *loc. cit.*; Fischer, *J. pr. Chem.* 1920, 100, 167) was prepared by the action of ammonia on the corresponding nitrosonaphthol, dissolving the product in dilute acid, reprecipitating with ammonia and crystallising from alcohol, when green needles were obtained.

β-Nitroso-α-naphthylamine (Harden, *loc. cit.*) was prepared by heating the corresponding nitrosonaphthol with ammonium chloride and crystallising the product from benzene, when green needles were obtained.

Both the reagents in alcoholic solution produced precipitates with Co, Cu and Ni only. Cobalt precipitation was done as follows.

Procedure.—A nickel-free cobalt chloride solution containing not more than 0.04 g. of cobalt was diluted to 300 c.c and buffered with sufficient sodium tartrate and acetate and the cobalt was precipitated with 1% alcoholic solution of the reagents. The mixture was boiled for about 20 minutes and allowed to stand for 15 minutes for complete setting and then filtered through a sintered crucible, washed first with dilute acid, then with dilute alkali and then made free from alkali with boiling water, dried at 110° for 1-2 hours and weighed. Exactly the same procedure was adopted in separating cobalt from other elements, but only the *α*-nitroso compound was used, it being very easily obtainable in sufficient quantity in the pure state. The precipitates were stable towards acid, alkali and organic solvents. A sample of the precipitate on analysis gave the following results. Nitrogen was estimated by Dumas method and cobalt was estimated as metallic cobalt.

(C₁₀H₇ON₂)₃Co requires : C, 62.93 ; H, 3.67 ; N, 14.68 ; Co, 10.31%

Found *α*-compound : C, 62.8 ; H, 3.67 ; N, 14.51 ; Co, 10.35%

β-compound : C, 62.3 ; H, 3.69 ; N, 14.52 ; Co, 10.38%

TABLE I.

Estimation of cobalt in solution containing or not containing other metal

Co taken.	M/10 Soln. of second metal taken	α -Reagent Co-ppt. obtained.	β Reagent Co-ppt. obtained.	Calc. wt.	Error (%)
0.01392 g	...	0.1351 g.	...	0.1350 g.	Nil
0.01392	...	0.1354	..	„	+0.3
0.02784	...	0.2703	...	0.2701	Nil
0.03481	...	0.3370	...	0.3377	-0.2
0.01392	0.1342 g	0.1350	-0.6
0.01392	0.1351	„	Nil
0.02784	0.2698	0.2701	-0.1
0.03481	0.3386	0.3377	+0.3
0.01392	5c.c. ZnSO ₄	0.1350	...	0.1350	Nil
0.01392	5c.c. Alum	0.1354	...	„	+0.3
0.01392	5c.c. Cr ₂ (SO ₄) ₃	0.1354	..	„	+0.3
0.02088	5c.c. MnSO ₄	0.2023	...	0.2025	-0.1

A much larger number of similarly accurate data have been actually collected, but they have not been included in the paper: These two reagents may be freely recommended for accurate estimation of cobalt and for its separation from other elements.

isoNitrosodimedone was prepared by the action of nitrous acid on dimedone and crystallising from aqueous solution by cooling with ice. The aqueous solution produced a precipitate only with cobalt and a slight colouration with nickel and copper. It produced a deep blue colour with iron. The cobalt precipitate was soluble in organic solvents and less stable towards acid than the naphthylamine precipitates. Its molecular weight was also found by the freezing point method to be 572,584,575 against 563, which is the calculated value for a cobaltic complex.

Procedure.—Cobalt solutions containing 0.01 to 0.1 g. or any greater amount was diluted to 200-300 c.c. and heated to 50° and cobalt precipitated with 1-2% aqueous solution of the reagent in slight excess. The temperature was then raised to 70-80° and kept at that range for 10 minutes and then the mixture was allowed to settle. This happened in about one minute. The precipitate was filtered through a sintered crucible, washed with

hot water, dried at 100° for 30-45 minutes and weighed. A sample on analysis gave the following results :—

$(C_8H_{10}O_3N)_3Co$ requires : C, 51.1 ; H, 5.32 ; N, 7.44 ; Co, 10.47%

Found : C, 51.8 ; H, 5.39 ; N, 7.65 ; Co, 10.32%

TABLE II:

Co taken.	Second metal taken	Ppt. obtained.	Calculated.	Error. (%)
0.03023 g	...	0.2883 g	0.2883 g.	Nil
0.03023	...	0.2887	,,	+0.15%
0.06046	...	0.5764	0.5766	Nil
0.09069	...	0.8649	0.8649	Nil
0.03023	0.02896 g. Ni	0.2883	0.2883	Nil
0.01511	,,	0.1446	0.1441	+0.3
0.03023	0.01647 g. Cu	0.2884	0.2883	Nil
0.01511	0.00295 g. Cu	0.1446	0.1441	+0.3
0.03023	5c.c.M/10ZnSO ₄	0.2880	0.2883	-0.1
0.03023	" " " MnSO ₄	0.2880	0.2883	-0.1
0.03023	" " " Alum	0.2884	,,	Nil
0.03023	" " " Cr ₂ (SO ₄) ₃	0.2884	,,	Nil

A large number of similarly satisfactory data have been omitted. Under proper care, this is the best reagent for quickest and exact estimation of cobalt and its separation from any mixture of metallic salts.

*Dinitrosoresorcinol and Dinitroso orcinol.**

These were prepared by the action of nitrous acid on the phenols. The resorcinol compound was crystallised from a saturated alcoholic solution by cooling. The orcinol compound could not be obtained in the crystalline state. They formed deep reddish brown precipitates with cobalt which are stable towards dilute acids.

Procedure :—(a) *With dinitrosoresorcinol*.—1 G. of reagent was dissolved in 100 c.c. of glacial acetic acid and diluted to 500 c.c. Cobalt

* (a) Orndorff & Nichols, *J. Amer. Chem. Soc.*, 1923 **45**, 1536

(b) Beilstein, II, 923, 568 and Kostanecki, *Ber.*, 1887, **20**, 31, 33

(c) Beilstein, VI, 883 (1923)

(d) Kostanecki, *Ber.*, 1887, **20**, 31, 33

solution containing 0.01-0.04 g. cobalt was diluted and heated to boiling and cobalt precipitated with requisite amount of the reagent and digested for 20 minutes and then after cooling was filtered through a sintered crucible under small suction, washed with 15% acetic acid and dried at 115° for 2-3 hours and weighed.

(b) *Dinitroso-orscinol*.—A 0.2% aqueous solution of the reagent was used. Precipitation was done as in the previous case and the precipitate which remained colloidal was coagulated with acetic acid and filtered and dried as previously. Results of estimations are not so accurate, both the complexes retaining a part of the reagents with great tenacity. Samples of the complexes gave the following results on analysis :—

Resorcinol complex requires : C, 36.63 ; H, 1.52 ; N, 14.3 ; Co, 15.01%
 $(C_6HO_4N_2)_2 Co$

Found : C, 37.00 ; H, 1.55 ; N, 13.9 ; Co, 15.2 %

Orcinol complex requires : C, 39.91 ; H, 2.37 ; N, 13.3 ; Co, 14.01%
 $(C_7H_5O_4N_2)_2 Co$

Found : C, 39.0 ; H, 2.33 ; N, 13.51 ; Co, 13.87%

TABLE III.

Co taken.	Ppt. obtained from resorcinol reagent.	Calc.	Error.
0.02945 g.	0.1960 g.	0.1964 g.	-0.2%
0.02945	0.1950	0.1964	-0.8
0.01472	0.0970	0.0982	-0.12
0.01472	0.0991	0.0982	+1
0.01472	0.1005	0.0982	+2.5
From orcinol reagent.			
0.02945	0.2100	0.2104	-0.2
0.02945	0.2121	0.2104	+2
0.02945	0.2116	0.2104	+2
0.01472	0.1042	0.1052	-1

These two reagents cannot be freely recommended for accurate estimation of cobalt or for its separation from other elements. The precipitates require a troublesome washing, as the reagents are very easily adsorbed by the precipitates.

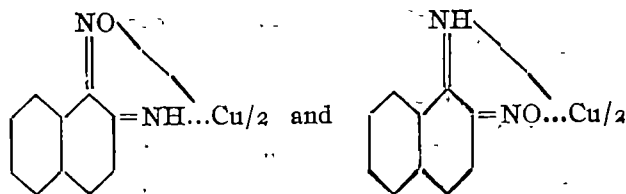
THE USE OF NITROSO DERIVATIVES AS REAGENTS IN INORGANIC ANALYSIS. PART II.

BY S. S. GUHA-SIRCAR AND SASANKA CHANDRA BHATTACHARYYA.

α - and β -Nitroso-naphthylamines are satisfactory reagents for the estimation of copper. Nickel also forms complexes with these reagents.

In Part I of this investigation, dealing with the quantitative estimation of cobalt, it has been mentioned that unlike the corresponding nitroso-naphthols α -nitroso- β -naphthylamine and β -nitroso- α -naphthylamine give copious precipitates with copper and nickel. We will deal with these metals one by one.

Precipitation of Copper.—With nitrosonaphthylamines copper forms inner complex salts which are chocolate in colour, the β -complex being of a deeper shade. The precipitates are quantitative and directly weighable, insoluble in organic solvents and in dilute alkali, but they are soluble in acids, the β -complex being somewhat more soluble than the α -complex. With these reagents copper has been estimated gravimetrically in the directly weighable state and has also been quantitatively separated from cadmium, aluminium, chromium, zinc and manganese. The precipitates are of definite composition and reveal the following constitution.



Found α -complex : C, 59.11; H, 3.47; N, 13.99; Cu, 15.6 %
 Found β -complex : C, 59.21; H, 3.40; N, 13.7; Cu, 15.57 %
 $(\text{C}_{10}\text{H}_7\text{N}_2\text{O})_2 \text{ Cu}$ requires: C, 59.23; H, 3.46; N, 13.82; Cu, 15.67 %

The copper solution containing 0.015-0.05g. of copper was diluted to 300 c.c. and 25 c.c. of 10% sodium-potassium tartrate were added. (Addition of tartrate was not essential when copper was estimated with α -nitroso compound. But tartrate should always be added when copper is estimated with the β -reagent and when it has to be separated from

other elements except cadmium). The solution was heated to boiling and the copper was thrown down with 1% alcoholic solution of the reagent. The solution was kept boiling for 20 minutes with constant stirring and then was allowed to settle. The precipitates were very granular and settled completely within a minute. The precipitation with the α -nitroso compound was always better and more satisfactory. The precipitate was then filtered through a sintered crucible, washed with a few c.c. of dilute alkali and then with boiling water and dried at 105° and weighed. It should be remembered that only the α -nitroso compound was used in cases of separations. Results are represented in Table I.

TABLE I.

Cu taken.	M/10 Soln. of 2nd metal taken.	Cu ppt.		Calc.	Error.
		α -Reagent.	β -Reagent.		
0.03295 g.	...	0.2106 g.	...	0.2103 g.	+0.1%
0.03295	...	0.2098	...	"	-0.2
0.01647	...	0.1052	...	0.1051	Nil
0.01647	...	0.1052	...	0.1051	Nil
0.03295	0.2110 g.	0.2103	+0.3
0.01647	0.1054	0.1051	+0.2
0.01647	0.1050	0.1051	Nil
0.03295	5 c.c. CdSO_4	0.2104	...	0.2103	Nil
0.03295	"	0.1056	...	0.1051	
0.01647	4 c.c. CdSO_4	0.1052	...	0.1051	Nil
0.01647	5 c.c. ZnSO_4	0.1054	...	0.1051	+0.3
0.03295	5 c.c. MnSO_4	0.2104	...	0.2103	Nil
0.01647	5 c.c. Alum	0.1054	...	0.1051	+0.25
0.01647	5 c.c. $\text{Cr}_2(\text{SO}_4)_3$	0.1055	...	0.1051	+0.3
0.01647	5 c.c. SbCl_3	0.1054	"	0.1051	+0.2
0.01647	...	0.1050	...	0.1051	Nil

As the results of estimations are very accurate, the reagents may be freely recommended for gravimetric estimation of copper and for its separation from other elements, particularly cadmium. The α -nitroso compound is comparable to, if not better than, the best of copper reagents at present used for quantitative estimation of the metal.

Precipitation of Nickel.

The process of estimation was the same as in the case of copper. But the results of direct weighing were not always accurate. The complexes were, therefore, filtered through gravimetric filter papers, washed as usual, dried, ignited and the residue on the crucible moistened with a few drops of nitric acid and then ignited again to nickelic oxide NiO and weighed. In separating from other elements, buffering with tartrate, prior to the precipitation, was essential. The α -complex was black and the β -complex was light chocolate in colour. They are not soluble in organic solvents and are less soluble in acids than the corresponding copper complexes.

TABLE II.

Ni taken	M/10-Soln. of the 2nd metal taken.	Wt. of nickel oxide		Calc.	Error.
		α -Reagent.	β -Reagent.		
0.02896 g.	0.0369 g.	0.0369 g.	Nil
0.02896	0.0368	0.0369	-0.3%
0.04054	0.0518	0.0516	+0.4
0.04054	0.0519	0.0516	+0.5
0.02896	5 c.c.M/10- ZnSO_4	0.0373 g.	...	0.0369	+1
0.02896	5 c.c.M/10- MnSO_4	0.0363	...	0.0369	-1.5
0.02896	5 c.c.M/10-Alum	0.0369	...	0.0369	Nil
0.02896	5 c.c.M/10- $\text{Cr}_2(\text{SO}_4)_3$	0.0374	...	0.0369	+1.3

The reagents are not entirely suitable or reliable for estimation.

A NEW METHOD OF PREPARATION OF ACETO- AND BENZONITRILES.

BY YHO SEIN GWAN.

p-Toluene sulphonyl chloride may be used as a dehydrating agent in the preparation of nitriles from acid amides. The advantage of the process is that the yield is better and the reagent is less drastic.

Benzonitrile.—Benzamide (12 g.) and dry *p*-toluenesulphonyl chloride (19 g.), were intimately mixed and heated under reflux at 130-35° (oil-bath) for 1½ hours. The mixture was then distilled in steam for the isolation of benzonitrile which was then redistilled (7.3 g.).

p-Toluenesulphonic acid can be recovered from the non-volatile residue.

Acetonitrile.—Similarly, acetamide (10 g.) gave with *p*-toluenesulphonyl chloride (31 g.) after interaction and isolation in the manner described, acetonitrile (5 g.).

Author's thanks are due to Drs. D.H. Peacock, J. Farquharson and Mr. B. K. Menon for their interest in the work.

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RANGOON.

Received January 13, 1941.

A NEW COLORIMETRIC METHOD FOR THE CHLORATE ION.

By M. B. Roy.

A new colorimetric method by using pyridine in concentrated H_2SO_4 producing permanent violet colour with chlorates, has been described for detection and rough estimation of small amounts of chlorates.

Only a few colorimetric methods are available for the detection of the chlorate ion. Virgili (*Ann. chim. anal. chim. appl.*, 1909, **14**, 85) suggested the use of aniline hydrochloride for detecting chlorates. A solution of aniline hydrochloride in hydrochloric acid at once develops a violet colour with chlorates, but it is not permanent and changes to blue. The method was improved by Jones (*Analyst*, 1931, **56**, 807). The test, however, is not specific for chlorate ions and cannot be applied in presence of other oxidising substances which also give the same colouration. Poch (*Anal. Fis. Quim.*, 1922, **20**, 662) reported a qualitative test for chlorate. The method depends upon the oxidation of ammonium thiocyanate by chlorate in specially prepared test paper with the production of a pale lemon-yellow to cadmium-yellow mixture of oxidation products of sulphocyanic acid. Offord (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 93) used this method for quantitative estimation of small amounts of chlorate in plant extracts. Halogens, bromate, iodate, persulphate, peroxide, and cupric salts, however, colour the thiocyanate test-paper similarly as chlorate.

The method described in the present paper was devised mainly for detecting small amounts of chlorate in presence of chloride. The method is based on the fact that a solution of pyridine in sulphuric acid produces a permanent violet colouration with chlorate. The test is best carried out as follows : 3 c.c. of pyridine is taken in a test tube and 9 c.c. of concentrated sulphuric acid are added to it drop by drop with constant shaking. When the liquid has cooled, the reagent is ready for use. If the substance to be examined is in solution, the solution containing chlorate is carefully evaporated to dryness in a small porcelain basin, as the colour is well developed with solid chlorates. A drop or two of the reagent is then added to the solid substance when an intense violet colour is produced which is quite permanent.

The colour produced varies from violet (0.01 to 1 mg. per c.c.) through deep violet (1 to 10 mg. per c.c.) to almost black (10 mg. per c.c. or over). It will be seen that the presence of chloride, bromide, iodide, perchlorate,

nitrate, persulphate, and phosphate does not interfere with the reaction. Coloured substances, such as chromate and dichromate, mask the colour of the chlorate test, and bromate and iodate give a colour similar to that developed by chlorate.

Although the test is mainly qualitative in nature, it may also be applied for quantitative estimation of small amounts of chlorate in absence of interfering substances with a fair degree of accuracy, because the intensity of shade developed is proportional to the quantity of chlorate present. In quantitative work it is advisable to prepare standards for matching the colour of the unknown, by evaporating solutions containing known amounts of potassium chlorate in small porcelain basins, and if the unknown contains a large amount of chlorate it should be dissolved in water and an aliquot part evaporated to dryness.

The method is useful in determining the amount of sodium chlorate in certain weed-killers, in which chlorides are used as diluents of sodium chlorate, sold in the market for the purpose. It is also applicable to the determination of chlorate in mixture with the ingredients of typical nutrient water cultures comprising nitrate, chloride, sulphate and phosphate, because none of these ions interfere with the reaction.

CHEMICAL EXAMINER'S LABORATORY, AGRA.

Received December 17, 1940

A NOTE ON CERTAIN HETEROCYCLIC SULPHONAMIDES.

BY U. P. BASU AND S. J. DAS-GUPTA.

In continuation of our previous investigations (Choudhury, Das-Gupta and Basu, *J. Indian Chem. Soc.*, 1937, **14**, 733; De and Basu, *Indian J. Med. Res.*, 1938, **26**, 537, Basu and Das-Gupta, *J. Indian Chem. Soc.*, 1939, **16**, 301) 2-sulphanilamido-4-methyl (Fosbinder and Walter, *J. Amer. Chem. Soc.*, 1939, **61**, 2032), and 2-sulphanilamido-3: 4-tetrahydrobenzothiazoles, and 4-sulphanilamido-1-phenyl-2:3-dimethyl-5-pyrazolone (Roblin, Williams and English, *J. Amer. Chem. Soc.*, 1940, **62**, 2002) have been prepared. But two of the above three compounds have already been published by the above authors. The method of preparation of the sulphamethyl-thiazole being somewhat different from that published and the tetrahydro-benzothiazole derivative being undescribed, our observations in this connection are recorded here. It has been found that neither the tetrahydrobenzothiazole, nor the sulphanilamidopyrazolone shows any activity against experimental pneumococcal (Type I) infections in white mice. The pharmacological investigations have been carried out by Dr. A. Bose and will be reported in detail elsewhere.

EXPERIMENTAL.

2-Amino-3:4-tetrahydrobenzothiazole.—2-Chlorocyclohexanone (1 mol.) and thiourea (1 mol.) were refluxed in absolute alcoholic solution for 1 hour and the alcohol distilled off. The residue was dissolved in water and the solution made strongly alkaline with potassium carbonate and extracted with ether. On evaporating the ether, the compound was isolated as a semi-solid mass, which was then converted into its hydrochloride by treating with hydrochloric acid. It separated as colourless crystals from rectified spirit, m.p. 243-44°. (Found: N, 14.04; Cl, 18.31. $C_7H_{10}N_2S$, HCl, requires N, 14.7; Cl, 18.63 per cent).

2-(p-Acetylaminobenzenesulphonamido)-3:4 tetrahydrobenzothiazole.—A solution of 2-aminotetrahydrobenzothiazole (3 g.) and *p*-acetylaminobenzenesulphonyl chloride (2 g.) in pyridine was left overnight. After distilling off the pyridine, the residue was washed with cold water and the compound obtained as buff-coloured microscopic crystals from a mixture of

alcohol and water (1:4), melting indefinitely at 180°. (Found: N, 11.2; H₂O, 4.7. C₁₅H₁₇O₃N₃S₂, H₂O requires N, 11.38; H₂O, 4.88 per cent).

2-Sulphanilamido-3:4-tetrahydrobenzothiazole.—*p*-Acetylamino benzene-sulphonamido-tetrahydrobenzothiazole (1 g.) was heated with aqueous alcoholic hydrochloric acid (5%, 20 c.c.) for 25 minutes. After treating the mixture as in the previous case, the compound was isolated as buff-coloured microscopic crystals from dilute alcohol, m.p. 150-54° (indifferent). (Found: N, 12.72; H₂O, 5.42. C₁₃H₁₃O₂N₃S₂, H₂O requires N, 12.84; H₂O, 5.5 per cent). The compound gives diazo reaction and is soluble in both acids and alkalis.

2-Sulphanilamido-4-methylthiazole.—A solution of *p*-acetylamino benzene-sulphonyl chloride (1 mol.) and 4-methylthiazole (2 mol.) in dry ethyl acetate was left overnight. The solvent was evaporated off and the residue obtained on treatment with cold water afforded the 2-(*p*-acetylamino benzene-sulphonamido)-4-methylthiazole already described by Fosbinder and Walter (*loc. cit.*) in a crystalline form. This product was hydrolysed by heating on a steam-bath with 5% hydrochloric acid in 50% alcohol (20 c.c. for 1 g.). The mixture was diluted with water and neutralised with ammonia in cold. The solid, separating, was isolated as buff-coloured microscopic crystals from 50% alcohol, m.p. 236-37°, yield 50% of the weight of the acetyl-derivative. (Found: N, 15.45. C₁₀H₁₁O₂N₃S₂ requires N, 15.61 per cent).

BENGAL IMMUNITY RESEARCH LABORATORY,
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Received January 16, 1941.

REVIEWS

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. PUBLISHED BY THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, FIFTH ED. 1940.

This is a revised edition of the well known book published by the Association of Official Agricultural Chemists on the standardised methods of analysis used in ordinary routine analysis and in research. The previous edition was published in 1936. In the present revised edition additions have been made on the following subjects :—Fish and other marine products, vitamins, microbiological methods and microchemical methods. The chapters on analytical methods begin with soil and subsequent chapters deal with the analysis of various materials like paints, varnishes and constituent materials, leathers, cereal foods, dairy products, eggs and egg products, meat and meat products, oils, fats and waxes, sugars and sugar products, vegetables and vegetable products, drugs etc. The previous editions of the book have been very useful to workers in analytical chemistry in choosing their methods of analysis and it is hoped that the present edition will be even more helpful to students of all branches of chemistry. The numerous reference tables given at the end of the book will serve as useful ready reference data to workers in chemical and in allied branches of science.

S.P.R.-C.

An Outline of Pharmacopoeial Drugs of Vegetable Origin. BY S. N. BAL, ED. 1940. PUBLISHED BY P. GHOSH & CO., COLLEGE ST., CALCUTTA. PRICE RE. 1-4-0.

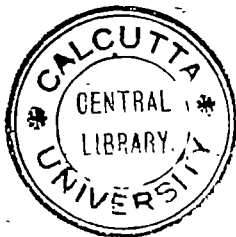
As given in the preface, this book presents in a short compass an account of the more important medicinal plants, which have been classified under the following heads :—

1. Plants numbering 96 recognised in British Pharmacopoeia.
2. Plants recognised in British Pharmaceutical Codex numbering 205 plants excluding that of British Pharmacopoeia.
3. Plants recognised by United States Pharmacopoeia but not mentioned in British Pharmaceutical Codex.
4. Plants used in Ayurvedic system of medicine. This list includes 165 plants, some of which also find mention in British Pharmaceutical Codex.

The need for such a treatise has been keenly felt by Pharmacologists and its timely appearance will be very welcome to the chemists and members of Medical profession, specially in India. The plants in the treatise have been arranged alphabetically according to their botanical names, but to facilitate references, indexes of common names of the plants have also been appended. The plants, which are found in India, either in wild state or in cultivation, have been marked with asterisks. The book is mainly intended for reference purposes. It is hoped that the book will prove extremely useful as a handy reference, not only to the students of pharmacy, but also to students of chemistry and of Botany. It will also be a source of interesting general informations to the scientifically minded public. In these days, when utilisation of national resources is considered to be extremely important, a knowledge of different varieties of Indian medicinal plants and their distribution will be very useful in the development of Indian pharmaceutical industry.

The printing of the book is excellent and considering the nature of the book, the price (Re. 1/4/-) is very moderate.

S. P. R.-C.





IODINATION. PART I. STUDIES ON THE EQUILIBRIUM IN SYSTEMS OF IODINE AND VARIOUS UNSATURATED ORGANIC COMPOUNDS IN THE DARK IN DIFFERENT NON-POLAR SOLVENTS.

By J. C. GHOSH, S. K. BHATTACHARYYA, M. M. DUTT AND M. J. RAO.

Investigations have been carried out on the thermal iodination of β -amylene and *dextro*-pinene in non-polar solvents like benzene, carbon tetrachloride and carbon disulphide. The reactions have been found to be reversible and the equilibrium constants have been determined under different experimental conditions.

The addition reactions of chlorine and bromine to unsaturated organic compounds have been studied in considerable details both in light as well as in the dark. But in comparison not much work has been done on addition reactions involving iodine in various polar and non-polar solvents. Such investigations, whether in the dark or in light, are troublesome, being for the most part very slow and disturbed by the incidence of a reverse reaction. Herz and Mylius (*Ber.*, 1907, **40**, 2898) found that in the reaction between allyl alcohol and iodine in the dark in solutions of carbon tetrachloride, chloroform and carbon disulphide, bimolecular constants were obtained in the individual experiments, but they varied considerably with the concentration. The same reaction was also studied by Caughley and Robertson (*J. Chem. Soc.*, 1933, 1323) both in the dark as well as in light in solutions of benzene, carbon tetrachloride and chloroform. But none of the above authors carried out the iodination of allyl alcohol in a systematic way—the last two authors carried out only one experiment in each solvent and concluded that the reaction was a simple bimolecular one. It is doubtful whether they would get bimolecular constants had they carried out the investigation in different concentrations of iodine. Another instance of iodination is the reversible formation and decomposition of ethylene iodide in the dark in solution of carbon tetrachloride studied by Polissar (*J. Amer. Chem. Soc.*, 1930, **52**, 956). Schumacher (*ibid.*, 1930, **52**, 3132) concluded that the reaction between iodine and ethylene in solution of carbon tetrachloride was homogeneous, proceeding by a chain reaction. Another example of iodination in the dark is the iodination of β -phenylpropionic acid in aqueous solution studied by Moelwyn-Hughes and Legard (*J. Chem. Soc.*, 1933, 424). But this reaction is complicated due to the presence of tri-iodide (I_3) ion formed by potassium iodide and iodine. Muller (*Bull. soc. chim.*, 1912, *iv*, **11**, 1006) studied the iodination of oleic acid in

carbon tetrachloride and ethyl acetate solutions at different dilutions and found bimolecular reaction in each case.

Bythell and Robertson (*J. Chem. Soc.*, 1938, 173) have studied the iodination of allyl alcohol, its acetate, benzoate and bromide and undecenoic acid, in different non-polar solvents, like carbon tetrachloride, hexane and chlorobenzene which form violet solutions and in polar solvents, like acetic acid and nitrobenzene, which form brown solutions. They observed that the reactions in polar solvents are homogeneous and termolecular and those in non-polar solvents are heterogeneous. The conclusion that the iodination in non-polar solvents is heterogeneous is reached by these authors as a result of the following observations :—

(i) When the reaction vessel is packed with glass beads, the reaction proceeds more rapidly and this increase may be very considerable—the rate may be increased 15-fold.

(ii) On reducing the concentration of the reactants, a region is reached where there is a rapid diminution in velocity.

(iii) There is a limiting temperature above which the adsorbed film becomes unstable with a rapid diminution in reaction rate.

Recently Ogg and Priest (*J. Chem. Phys.*, 1939, 7, 736) have shown that thermal as well as photochemical reactions between iodine and cyclopropane in the gas phase are homogeneous and proceed by a chain reaction started by iodine atoms.

The most important investigations in this field were made by Gróh and Szelestey (*Z. anorg. Chem.*, 1927, **162**, 333) who studied the iodination of erucic acid $[\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}]$ in the dark in solutions of carbon tetrachloride and carbon disulphide at 35° , 15° and 13.8° . They found that the reaction velocity is proportional to the concentration of acid and to the cube of the iodine concentration, i.e. that the active molecule is I_3 . The reaction is expressed as $\text{I}_3 + \text{E} \rightleftharpoons \text{EI}_3 + 2\text{I}_2$. In neither solvent is the reaction complete, the equilibrium constant for carbon disulphide being 7.76 and for the carbon tetrachloride solution 19.8 at temperature 25° . The reaction velocity diminishes with rise in temperature. Gróh and Takacs (*Z. physikal. Chem.*, 1930, **149**, 195) have studied the decomposition of erucic acid di-iodide and found that it is catalysed by iodine according to the equation,

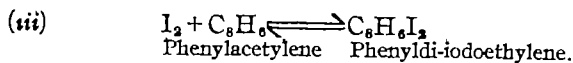
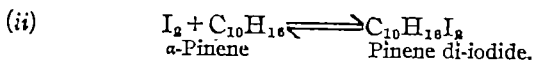
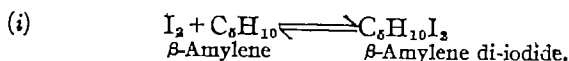


The above authors gave convincing proof of their mechanism of the above reaction by showing that the velocity constant of decomposition found

experimentally according to the above reaction scheme was almost equal to that calculated from known equilibrium constant and the velocity constant of the formation of the di-iodide.

Thus we see that addition reactions involving iodine to unsaturated organic compounds in non-polar and polar solvents are complicated and full of controversy.

In this part and in subsequent parts* (II and III), we shall describe the results of investigations made on the thermal iodination of β -amylene, d -pinene and phenylacetylene in non-polar solvents, like benzene, carbon tetrachloride and carbon disulphide and in polar solvents, like acetic acid and ethyl alcohol. The reactions are reversible and do not proceed to completion. The reactions can be represented according to the equations :—



Iodine reacts with β -amylene both in the dark as well as in light. When the concentration of iodine is less $\{[\text{I}_2] < 0.02M\}$, the thermal reaction is immeasurably small but the reaction proceeds fast in light ; but when $[\text{I}_2] > 0.02M$, there is an appreciable thermal reaction. The reaction between iodine and phenylacetylene in the dark in non-polar solvents is extremely small even with high initial concentrations of iodine, whereas it proceeds very fast in light.

In alcoholic solution there is an appreciable dark reaction with higher concentrations of iodine which becomes *nil*, when the concentration of iodine is low $< 0.025M$.

In this part results of investigations on the equilibrium in systems I_2 — β -amylene and I_2 —pinene in the dark have been described.

EXPERIMENTAL.

Reagents.—Merck's extra pure carbon tetrachloride, benzene and carbon disulphide, which were used in these investigations were further purified by allowing them to stand over fused CaCl_2 for three days and by subsequent distillation. Merck's resublimed iodine was used after

* To be published in the next issue (Issue No. 5).

further sublimation. B.D.H. purest β -amylene and Kahlbaum's *dextro*-pinene, further purified by distillation, were used in these investigations. β -Amylene forms peroxides in contact with air; so fresh solutions were prepared with freshly distilled acceptor after every two days so that no appreciable amount of peroxide was formed to vitiate our results.

Thermal Equilibrium.—The equilibria were studied at two different temperatures. For this purpose two series of reaction mixtures were kept in sealed glass tubes in each solvent. One series was kept in a bath at room temperature and the other series in a frigidaire. The initial concentration of iodine in each was determined and after two months, when equilibrium was attained, the concentration of iodine at equilibrium was determined in each case. The equilibrium constant K_x was calculated according to the relation,

$$K_x = \frac{[AI_2]_x}{[A]_x [I_2]_x}$$

where $[A]_x$, $[I_2]_x$ and $[AI_2]_x$ are the concentrations of the acceptor, iodine and the di-iodide at equilibrium.

The experimental data are recorded in Tables I-III, in which a and b denote initial concentrations of iodine and the acceptor respectively in g. mols/litre; a_x (0°), a_x (30°), a_x (27°) denote concentrations of iodine at equilibrium at 0° , 30° and 27° respectively and K_x , the equilibrium constant.

TABLE I

Acceptor— β -amylene.

Solvent.	b (mol.)	a (mol.)	a_x (0°). (mol.)	a_x (30°). (mol.)	K_x .	
					0° .	30° .
CCl ₄	0.1	0.0928	0.0516	0.065	13.58	5.92
	0.05	0.053	0.0372	0.0429	12.43	5.90
	0.025	0.0265	0.0213	0.0237	12.32	5.32
					Mean 12.78	5.71
C ₆ H ₆	0.198	0.110	0.0438	0.0630	11.48	4.94
	0.099	0.110	0.0625	0.0840	14.76	4.24
	0.148	0.055	0.0223	0.0363	12.72	3.98
					Mean 12.99	4.39
CS ₂	0.0444	0.0689	0.0567	0.0612	6.67	3.44
	0.178	0.103	0.0526	0.0703	7.51	3.20
					Mean 7.09	3.32

TABLE II.

Acceptor—pinene.

Solvent.	b. (mol).	a. (mol).	$a_E (0^\circ)$. (mol)	$a_E (27^\circ)$. (mol).	K_E	
					0° .	27° .
CCl ₄	0.0400	0.04	0.013	0.0179	159.76	69.06
	0.0385	0.027	0.00655	0.0106	173.0	70.00
					Mean 166.38	69.53
C ₆ H ₆	0.021	0.0217	0.0123	0.0142	65.88	39.13
	0.042	0.0434	0.0188	0.0230	75.19	41.06
					Mean 70.54	40.09
CS ₂	0.02	0.0211	0.0106	0.0132	104.2	49.45
	0.04	0.0423	0.0170	0.0230	101.3	40.54
					Mean 102.75	44.99

Heat of Reaction from Equilibrium Data.

The heat of reaction Q_v can be calculated from Vant Hoff's Isochore,

$$\frac{d \log K_E}{dT} = \frac{Q_v}{RT^2}$$

which on integration gives the expression,

$$\log K_E(T_1) - \log K_E(T_2) = \frac{Q_v}{R} \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

where $K_E(T_1)$ and $K_E(T_2)$ are the equilibrium constants at temperatures T_1° and T_2° absolute ($T_1 > T_2$); Q_v is the heat of reaction and R , the gas constant.

In the following table the heats of reaction between iodine and β -amylene and between iodine and d -pinene in different solvents are given.

TABLE III.

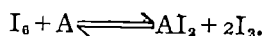
Solvent.	K_E $\theta = 0^\circ$	K_E $\theta = 30^\circ$	Q_v . (calories)	K_E $\theta = 0^\circ$	K_E $\theta = 27^\circ$	Q_v . (calories).
	β -Amylene.			d -Pinene		
CCl ₄	12.78	5.71	-4443.0	166.38	69.53	-5291.0
C ₆ H ₆	12.99	4.39	-5984.0	70.54	40.09	-3427.0
CS ₂	7.09	3.32	-4185.0	102.75	44.99	-5012.0

DISCUSSION.

The reactions have the following characteristics:—

The equilibrium constant is independent of the initial concentrations of iodine and the acceptor but depends on temperature. With rise in temperature the constant diminishes rapidly which means that the reactions are exothermic. The heat of reaction is of the order -4000 to -6000 calories in the reaction between iodine and β -amylene and of the order -3000 to -5000 calories in the case of pinene.

In Part II of the series, it will be shown that the velocity of the addition of iodine to β -amylene and pinene in the dark is proportional to the concentration of the acceptor and to the cube of the iodine concentration, *i.e.*, the active molecule is I_3 , so that the reaction may be represented according to the equation,



Hence,

$$\begin{aligned} \frac{dx}{dt} &= k''[I_3][A] - k'[AI_3][I_2]^2 \\ &= k[I_2]^3[A] - k'[AI_3][I_2]^2. \end{aligned}$$

At equilibrium,
so that,

$$k[I_2]_e^3[A]_e = k'[AI_3]_e[I_2]_e^2$$

$$K_e = \frac{k}{k'} = \frac{[AI_3]_e [I_2]_e^2}{[I_2]_e^3 [A]_e} = \frac{[AI_3]_e}{[I_2]_e [A]_e}$$

where K_e is the equilibrium constant.

This relation has been found to hold good.

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Received February 2, 1941.

ELECTRODEPOSITION OF CADMIUM ON IRON.

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Results are given for the optimum conditions for the production of a smooth and adherent deposit of cadmium on iron in respect of inter-electrode distance, the electrolyte concentration, the current density, the duration of electrolysis, the temperature, proportion of free sulphuric acid and of sodium sulphate. Data are also given for the cathode efficiency in respect of cadmium deposition under the influence of the above factors and that of the addition of a large number of inorganic and organic agents in different proportions, e.g., stannous chloride, aluminium sulphate, dextrin, gelatin, etc. The possible rôle of these addition agents is also discussed in the light of the current theories.

The coating of cadmium is superior to that of zinc for protecting iron and steel as it is less susceptible to atmospheric corrosion. In contrast to the dull appearance of zinc it is white and lustrous, almost like silver. These and the like were some of the remarkable properties of cadmium, which attracted the attention of the metallurgist. A review of the literature shows that much of the work on cadmium deposition is restricted to the use of double cyanide solutions, which are, however, unstable and therefore, apt to undergo decomposition; this leads to many practical difficulties in maintaining the satisfactory control of the plating bath. The work of Mary Dover (*J. Amer. Chem. Soc.*, 1911, **33**, 1577) and of Mary Holmes and Mary Dover (*ibid.*, 1910, **32**, 1251) has shown that cadmium can be deposited in a satisfactory and adhesive form from various organic electrolytes, viz., lactate, acetate, formate, etc., by using a rotating spiral anode, under conditions of (a) low current, and (b) decidedly acidic medium. It was observed that each of the above electrolytes exerted a marked and specific influence on the character of the deposit; the best deposits were obtained in presence of a mixture of ions and especially of $\text{SO}_4^{''}$ ion. A detailed account of the various baths for cadmium deposition is found in an exhaustive review by Mathers and Marble (*Trans. Amer. Electrochem. Soc.*, 1914, **26**, 297, 319). Their results show that alkaline and ammoniacal tartrate baths give very loose and spongy deposits. The baths containing the sulphates and chlorides, when used singly, did not give satisfactory results, though the latter yielded satisfactory deposits especially in the presence of NH_4Cl , free HCl and suitable addition agent. Excellent results were also obtained from solutions of fluoride, silicofluoride, borofluoride (*cf.* also Millian, *Bull. soc. chim. Belg.*, 1925, **34**, 143) and perchlorate (*cf.* Müller and Barchamann, *Z. Electrochem.*, 1933, **39**, 341) in presence of free acid and suitable addition

agent. With the exception of the work by Wernick (*Trans. Amer. Electrochem. Soc.*, 1932, **62**, 75) the information available in the literature on the quantitative data for cadmium deposition is very meagre. In the present investigation an attempt has, therefore, been made to study the deposition of cadmium on iron quantitatively in regard to the influence of a number of factors (*vide infra*).

EXPERIMENTAL.

The electrolysis was carried out in a round glass trough, about 2½" deep, and having a capacity of about 200 c.c., kept immersed in a thermostat and maintained at the desired temperature. The temperature of the bath solution was controlled within $\pm 0.2^\circ$. The anode used was a well cleaned thick plate of pure cadmium of size 4×4 cm. A thin plate (4×3.5 cm. approx.) serving as the cathode was first rendered free from grease by dipping it in a hot 10% caustic soda solution for a few minutes and then washing it with water; it was next immersed in moderately strong nitric acid to remove surface scales and rust and to loosen the coating of carbon. It was then well washed with water and was made an anode in the etching solution (100 g. H_2SO_4 and 100 g. Na_2SO_4 in 1000 c.c. water) and current was passed for half an hour. The plate was made an anode to prevent it from becoming brittle owing to the occlusion of hydrogen evolved at the cathode. This gave an uniformly etched and bright surface. The plate was then washed with distilled water and finally with alcohol, dried and weighed accurately. A copper coulometer was used to give the measure of the quantity of electricity passed through the electrolyte; the coulometer solution was prepared according to Ottel's recommendations (*Chem. Ztg.*, 1893, **17**, 543). The current was obtained from storage cells; the circuit included an electrolytic bath, copper coulometer, a precision type ammeter, and an adjustable resistance in series and voltmeter, connected across the electrodes in the bath.

The stock solution of 8% cadmium was prepared by dissolving 182.5 g. of Merck's pure cadmium sulphate, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, in 1000 c.c. of distilled water. In all the following experiments this stock solution was used either alone or after proper dilution or with the appropriate additions of the other materials used in this work. The concentration of cadmium sulphate in the solutions used, is expressed, for the sake of convenience, in terms of the metal content only. To investigate the optimum conditions for a smooth, bright and adherent deposit of cadmium, the influence of the following factors has been studied over ranges;

	Optimum values.
(a) Inter-electrode distance, 3 to 6.5 cm.	6 cm.
(b) Concentration of cadmium sulphate, 8 to 2% Cd.	4% Cd.
(c) Current density, 1.75 to 11.56 amp./ft ² .	5 amp./ft ² .
(d) Time, 10 to 60 min.	20 minutes.
(e) Free sulphuric acid, N/50 to N/4.	N/50 acid.
(f) Sodium sulphate, 1 to 10%.	5% Na ₂ SO ₄

The influence of C.D. and temperature on the nature and quantity of the deposit has been studied in a greater detail. Measurements were made of the cathode efficiency for the Cd-deposition at 30° under these conditions and in the presence of (i) inorganic agents, viz., Al₂(SO₄)₃, 18H₂O; NiSO₄, 7H₂O; H₂O₂; ZnSO₄, 7H₂O; HgCl₂; CrO₃; SnCl₂; SnO; SnO₂ and traces of SnCl₄, BiCl₃; (ii) organic agents, viz., sucrose, glycerine, dextrin, gelatin and traces of carbon disulphide and pyridine. The nature of the cadmium deposit obtained in each of these experiments is also recorded, as examined with a microscope. The cathode efficiency in any given experiment was calculated by the relation,

$$\% \text{ Cathode efficiency} = \frac{100 \times \text{equiv. wt. of Cu} \times \text{wt. of Cd deposited}}{\text{Equiv. wt. of Cd} \times \text{wt. of Cu (coulometer) deposited}}$$

TABLE IA.

Variation of inter-electrode distance.

Conc.=8% Cd as sulphate. Temp.=25°. C. D.=10 amps./sq. ft.
Time=20 min.

Electrode distance	Nature of the deposit.
3 cm.	Deposit fine, non-adhesive and gets washed off easily; 'tree' forming tendency at the edges.
5.0	Deposit finer, 'tree' forming tendency at the edges, non-adhesive but shining.
6.0	Deposit still finer and adherent, very fine crystals, no 'tree' formation.
6.5	Do.

TABLE IB.

Variation of concentration of the electrolyte (CdSO₄).

Temp.=25°. C. D.=5.5 amps./sq. ft. Inter-electrode distance=6 cm.
Time=20 min.

Conc. of CdSO ₄	Nature of the deposit.
8% Cd	Irregular crystals, fine and shining.
4	Regular and smooth crystals; deposit uniform and fine grained though adherence was not satisfactory.
2	Deposit shining and lustrous; 'tree' forming tendency at the edges

TABLE IC.

Variation of current density.

Conc. = 4% Cd as sulphate. Temp. = 25°. Inter-electrode distance = 6 cm.

Time = 20 min.

C. D. per sq. ft.	Nature of the deposit.
1'75 amp.	Deposit crystalline, shining but granular with deep holes.
3'66	Improvement in structure.
5'64	Deposit very fine, regular crystals; much improvement in structure.
7'73	Do.
9'43	Improvement in structure, but 'tree' formation at the edges.
11'56	Do.

TABLE ID.

Variation with time.

Conc. = 4% Cd as sulphate. C. D. = 5 amp./sq. ft. Inter-electrode distance = 6 cm. Temp. = 25°. The same bath solution used for all expts.

Time.	Nature of the deposit
10 min.	Deposit shining and lustrous, fine-grained and of uniform structure.
15	Do.
20	Slight improvement.
30	Do.
60	Deposit shows tendency to become spongy, powdery and black from the commencement of the electrolysis. The deposit being non-adherent, falls to powder on mere tapping the plate.

TABLE IE.

Effect of addition of free sulphuric acid to the bath.

Conc. = 4% Cd as sulphate. C. D. = 5 amp./sq. ft. Inter-electrode distance = 6 cm. Temp. = 30°.

Conc. of H_2SO_4 .	Nature of the deposit	% Cathode efficiency of Cd.
0	...	96'49 } 98'24 } 97'37
N/50	Deposit white, lustrous, crystalline, granular & coarse with little pitting effect.	93'89 } 94'21 } 94'05
N/20	Do.	90'46 } 88'44 } 89'7
N/10	Less uniform, increased pitting effect.	68'24 } 68'85 } 68'55
N/4	Deposit bad with deep holes and cracks	25'07 } 24'72 } 24'89

TABLE IF.

Effect of the addition of sodium sulphate.

Bath composition = 4% Cd as $\text{CdSO}_4 + \text{N}/50 \text{ H}_2\text{SO}_4$. Time = 20 min.
 Inter-electrode distance = 6 cm. Temp. = 30° . C. D. = 5 amp./sq. ft.

Na_2SO_4 .	Nature of the deposit.	% Cathode efficiency of Cd.
1%	Deposit white, lustrous but irregular with pitting effect; adherence poor.	91'77 } 91'71 } 91'74
2.5	Deposit lustrous, regular and adherent; pitting effect less.	92'42 } 92'77 } 92'60
5.0	Deposit much improved in structure being regular and uniform; very little pitting effect.	96'70 } 96'92 } 96'86
10	Do. No marked improvement.	97'44 } 98'56 } 98'0

TABLE II.

Effect of current density.

Bath soln. = 4% Cd as $\text{CdSO}_4 + \text{N}/50 \text{ H}_2\text{SO}_4 + 5\% \text{ Na}_2\text{SO}_4$.
 Inter-electrode distance = 6 cm. Temp. = 30° . Time = 20 min.

C. D. per sq. ft.	Wt. of Cd deposit.	Wt. of Cu (coulometer deposit).	% Cathode efficiency (mean).	Remarks.
1.0 amp	0'0451 g. 0'0328	0'0278 g. 0'0204	91'77 } 90'95 } 91'37	Deposit adherent but dull and not regular.
5.0	0'0781 0'0730	0'0458 0'0426	96'70 } 96'92 } 96'81	Deposit adherent, lustrous & uniformly fine-grained.
10.0	0'1196 0'0898	0'0695 0'0521	97'34 } 97'50 } 97'42	Fine-grained & lustrous deposit but non-adherent with 'tree' formation at the edges.
15.0	0'1273 0'1482	0'0733 0'0840	98'22 } 99'79 } 99'01	Do.

TABLE III.

Effect of temperature.

Bath soln. = 4% Cd as $\text{CdSO}_4 + N/50 \cdot \text{H}_2\text{SO}_4 + 5\% \text{Na}_2\text{SO}_4$. Inter-electrode distance = 6 cm. C. D. = 5 amps./sq ft. Time = 20 min.

Temp.	Wt. of Cd deposit.	Wt. of Cu (coulometer deposit).	%Cathode efficiency of Cd.	Remarks.
10°	0.0646 g.	0.0407 g.	89.78	Deposit adherent, regular & fine grained; pitting effect very little.
	0.0600	0.0380	89.32	
20°	0.0554	0.0339	92.43	Do.
	0.0541	0.0329	93.01	
30°	0.0781	0.0458	96.70	Deposit uniformly lustrous, regular & adherent with very little crevices.
	0.0730	0.0426	96.02	
45°	0.0700	0.0406	97.52	Do. little pitting effect.
	0.0574	0.0332	97.79	
60°	0.0652	0.0387	95.28	Deposit not uniform, less adherent but bright with crevices.
	0.0767	0.0455	95.35	
80°	0.0603	0.0356	93.76	Do. deep crevices
	0.0556	0.0338	93.05	

TABLE IV.

Effect of addition agent.

Bath soln. = 4% Cd as sulphate + $N/50 \text{H}_2\text{SO}_4 + 5\% \text{Na}_2\text{SO}_4$.

Inter-electrode distance = 6 cm. Time = 20 min.

Temp. = 30°. C.D. = 5 amp./sq ft.

Addition agent. (A)	Amount of (A) in 100 c.c. soln.	Wt. of Cd deposit.	Wt. of Cu (coulometer).	%Cathode efficiency.	Remarks.
$\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$	0.25 g.	0.0590 g.	0.0345 g.	96.74	Fine-grained and white deposit but not lustrous and adherent.
"	"	0.0553	0.0325	96.23	
"	0.5	0.0561	0.0329	96.45	Deposit finer and better than in previous reading.
"	"	0.0541	0.0320	95.63	
"	"	0.0582	0.0341	96.51	

TABLE IV (contd.)

Addition agent ^t . (A)	Amount of (A) in 100 c.c. soln.	Wt. of Cd. deposit.	Wt. of Cu (coulom- eter).	%Cathode efficiency.	Remarks.
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	1.0 g.	0.0738 g.	0.0436 g.	95.74	95.70 } Deposit improved in all respects
"	"	0.0504	0.0298	95.66	
"	1.5	0.0744	0.0439	95.86	95.56 } Still further improved but slight blackening effect.
"	"	0.0755	0.0449	95.26	
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.1	0.0574	0.0343	94.64	94.93 } Improvement in the deposit in all respects.
"	"	0.0616	0.0366	95.22	
"	0.2	0.0608	0.0364	94.47	94.55 } Do.
"	"	0.0604	0.0361	94.63	
"	0.5	0.0759	0.0459	93.53	93.26 } Still improved.
"	"	0.0485	0.0295	92.99	
HgCl_2	0.1	Black, powdery and non-adherent deposit
CrO_3	0.2	Do.
CS_2	1 drop	Do.
Pyridine	1 drop	91.17	91.11 } Deposit shining uniform, irregular and granular.
				91.06	
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.1 g	0.0516	0.0306	95.38	95.59 } No distinct improvement.
"	"	0.0490	0.0289	95.8	
"	0.5	0.0560	0.0332	95.4	95.27 } Irregular, granular and crystalline deposit with diseased spots.
"	"	0.0360	0.0214	95.15	
H_2O_2	0.1 c.c.	0.0506	0.0309	92.62	92.4 } Deposit non-uniform, lustrous, granular in structure with deep crevices
"	"	0.0585	0.0359	92.17	
"	0.5	0.0596	0.0345	97.68	97.97 } Deposit irregular and less satisfactory; worse than in previous case
"	"	0.0597	0.0344	98.17	
SnCl_2	0.009 g	0.0849	0.0499	96.23	97.15 } Deposit uniform shining and adherent.
"	"	0.0629	0.0363	98.07	
"	0.1	0.0759	0.0436	98.46	Deposit white amorphous and uniform; no pitting effect, no crevices, very good deposit.
"	0.11	0.0573	0.0327	99.13	99.1 } Do. very satisfactory.
"	"	0.0613	0.0350	99.09	

TABLE IV (contd.).

Addition agent. (A)	Amount of (A) in 100 c.c. soln.	Wt of Cd. deposit.	Wt. of Cu (coulom- eter).	%Cathode efficiency.	Remarks.
SnO	0.1 g.	0.0549 g	0.0327 g.	94.97	95.38 Granular, crystalline and coarse deposit with deep crevices and diseased spots.
"	"	0.0537	0.0317	95.8	
SnO ₂	0.1	0.0484	0.0284	96.38	96.49 Do. Structure somewhat better than in the previous case.
"	"	0.0521	0.0305	96.60	
SnCl ₄	A pinch	Deposit crystalline, coarse and diseased spots			granular, with crevices and diseased spots
SbCl ₃	"	Deposit spoiled, black, non-adherent and powdery.			
BiCl ₃	"	Deposit amorphous and adherent with "tree" forming tendency and blackening effect.			
"	In micro quantity.	Considerable improvement in the deposit.			
Gelatin	0.003 g.	0.0539 g.	0.0318 g.	95.87	95.57% Deposit white dull, amorphous, uniform and adherent.
"	"	0.0489	0.0290	95.27	
"	0.010	0.0610	0.0362	95.30	95.75 Improvement in the deposit.
"	"	0.0643	0.0378	96.20	
"	0.050	0.0591	0.0341	98.03	97.6 Further improved.
"	"	0.0691	0.0402	97.2	
"	0.10	0.0572	0.0343	94.33	94.63 Deposit further improved.
"	"	0.0621	0.0370	94.93	
Dextrin	0.1	0.0627	0.0368	96.37	96.09 Fine, uniform, shining, crystalline deposit; no pitting effect.
"	"	0.0813	0.0480	95.80	
"	0.25	0.0604	0.0353	96.50	96.28 Finer deposit but crystalline.
"	"	0.0625	0.0368	96.06	
"	0.50	0.0577	0.0338	96.60	96.88 Improvement in the deposit.
"	"	0.0838	0.0489	96.99	
"	1.0	0.0678	0.0400	95.90	95.8 Still improved.
"	"	0.0697	0.0412	95.70	
Glycerine	0.5 c.c.	0.0676	0.0402	95.10	95.24 Deposit not uniform, crystalline with diseased spots.
"	"	0.0501	0.0297	95.38	
"	1.0 "	0.0524	0.0318	93.30	93.2 Slight improvement in the deposit.
"	"	0.0461	0.0280	93.11	
Sucrose	5.0 g.	0.0667	0.0397	95.01	94.71 Deposit non-uniform, irregular, granular, coarse and crystalline with pitting effect and diseased spots.
"	"	0.0596	0.0357	94.41	
"	10.0	0.0578	0.0348	93.90	93.69 Not much improvement.
"	"	0.0608	0.0368	93.43	

DISCUSSION.

The foregoing results show that the nature and magnitude of an electrodeposit is influenced by a number of physicochemical factors. These are discussed conveniently in respect of cathode efficiency which is 100% under ideal conditions. Its diminution is chiefly due to the occurrence of side reactions, *e.g.* evolution of hydrogen at the cathode, or the formation of molecular or ionic complexes in the conducting mixture.

The process of electrodeposition, according to Smee, is essentially a process of crystallisation and laws of crystallisation are applicable to the electrodeposited metal. The deposition of metal consists initially of the formation of nuclei at the cathode surface followed by their growth to larger crystals. The two processes take place side by side. Each of these has a different velocity. If the velocity of (1) nuclei formation is greater than that of (2) crystal formation, a fine deposit is obtained, whereas in the reverse case the deposit is coarser and crystals big. The relation between the velocities of (1) and (2) depends, besides the factors mentioned, *i.e.* (a) to (f) (*vide supra*), upon (g) temperature, (h) nature of solvent, (i) nature of the metal deposited, and (j) its valency.

Our results in Table IA show that with the increase of electrode distance the deposit becomes finer. Adhesivity is also improved. From our results in Table Ic it is seen that with increase in C.D., the deposit becomes finer and adherent up to a particular limit after which it shows a distinct 'tree'-forming tendency, especially at the edges. Similar were the conclusions of Wernick (*loc. cit.*) who demonstrated that the increase in C.D. decreases appreciably the grain size and improves adhesivity and burnishability of the cadmium deposit from the sulphate bath containing boric acid and sodium chloride. At C.D. above 4.5 amps. per sq. dm. he observed that the 'tree' formation was more prominent even with a violently agitated solution. Watanabe and Tsuchimolo (*J. Min. Met. Japan*, 1929, 7, 3, 34) noticed the same effect with cyanide bath and that C.D. necessary for giving good and satisfactory deposit largely depends upon the concentration of the bath. These changes in the nature of the deposit are consistent with the fact that at very low C.D. or with very dilute solutions, the discharge of metal ions occurs slowly and so the rate of crystal formation exceeds that of nuclei formation, thus resulting in a coarse and crystalline deposit. At higher C.D., the rate of nuclei formation increases and the deposit becomes finer-grained. 'Tree' formation or burning effects observed, especially at very high C.D., can be attributed either to the local impoverishment of the metal or metal ion content round the cathode surface due to rapid depletion of the metal during the

electrolysis, or to the formation and subsequent inclusion in the cathode deposit, of hydroxides or basic salts of the metal due to increased alkalinity of the bath, caused by excessive hydrogen evolution.

FIG. 1.

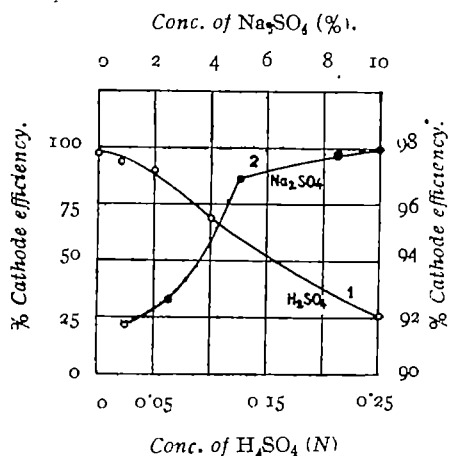
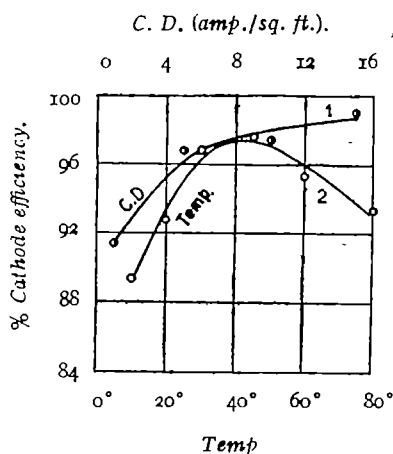


FIG. 2.



Our data recorded in Table II (*cf.* curve 1, Fig. 2) show that the cathode efficiency is very high even at low C.D. and in fairly high acidic media; it increases, though within very narrow limits (91.4 to 99%), continuously with the rise of C.D. possibly due to increase in hydrogen overvoltage and corresponding diminution in hydrogen evolution. The C.D., however, does not seem to have a marked influence over the cathode efficiency (*cf.* Wernick, *loc. cit.* Watanabe and Tsuchimolo, *loc. cit.*) in cadmium deposition as is noted to have in nickel deposition (results to be published shortly), where the efficiency alters within wide limits (0 to 100%). This remarkable difference in the behaviour of cadmium and nickel under low and high C.D. can be accounted for the hydrogen evolution at the cathode being usually the main cause leading to a deficit in the cathode deposit. The possibility of the hydrogen ions being discharged along with or in preference to metallic ions is dependent not only upon the relative position of the metals (such as cadmium and nickel) in the electrochemical series, and the concentration of H^+ ions and of metal ions in the electrolyte, but also upon the extent of irreversibility (Allmand and Ellingham, "Principles of Electrochemistry", 1931, p. 116) involved in the deposition of the metal and of hydrogen under any given set of conditions. Thus, though cadmium is a baser metal than nickel, yet it can be cathodically deposited from a solution containing much acid,

with high current efficiency, whereas nickel may not be deposited at all from a solution of corresponding concentration in metal ions and H^+ ions.

It is interesting to note that at constant values of C.D., concentration, temperature, etc., the deposit, which was initially bright and adherent, tends to become, as the time elapses, loose, powdery, non-adhesive and black (*cf.* Table Id). This can be attributed to the increased alkalinity of the bath due to high anodic efficiency of cadmium anode (more than 100%), with the progress of electrolysis and subsequent inclusion of the basic hydroxides in the cathode deposit. Kurda's findings (*Z. physikal. Chem.*, 1936, 178, 377) lead to similar conclusions.

Our results in Table Ix show that the addition of free sulphuric acid (N/50) to the bath solution improves considerably the nature and quality of the deposit, as examined microscopically. Increased concentration of the acid, however, besides lowering the cathode efficiency to a considerable extent (97.4 to 25.9%, *cf.* curve 1, Fig. 1) owing to excessive hydrogen evolution, gives 'cracked' and 'pitted' deposits with deep crevices. Results with the addition of Na_2SO_4 (*cf.* Table Ix) to the bath show that both the quality and quantity of the deposit get very much improved with increased amount of added material, upto 5%, and then remain almost unaffected with 10%. The sudden inflexion in the cathode efficiency-sodium sulphate concentration curve (curve 2, Fig. 1) corresponding to 5% sodium sulphate yielding smooth and satisfactory deposit, may possibly be attributed to the existence of a complex salt, $Na_2[Cd(SO_4)_2]$ in the plating solution. The solutions containing complex salts are known to give satisfactory and better deposits than those containing simple salts. The favourable results obtained can, in general, be attributed to sodium sulphate acting either as a conducting salt or as a bath stabiliser owing to its buffer action. This stabilising influence of Na_2SO_4 seems to have been noticed earlier by Westbrook (*Amer. Electrochem. Soc.*, 1929, May, advanced copy) who concludes that various substances like NaCN, NaOH, Na_2SO_4 added to the cyanide bath increase the conductivity and stability of the bath, raise the cathodic current efficiency, throwing power and maximum C.D. for satisfactory deposition and give smoother and finer grained deposits. He further adds that the presence of Na_2SO_4 hardly affects the electrical properties of the bath but seems to render it more stable. Because of common SO_4^{--} ion in $CdSO_4$, H_2SO_4 , and Na_2SO_4 the metal ion content of the bath solution is depressed to a considerably low value, a condition which is favourable for good and fine deposit.

From a study of the data, shown in Table III, it is seen that at constant C.D., the quality and quantity of the deposit (*cf.* curve 2, Fig. 2) improve

by increasing the temperature up to a certain extent (about 45°) and deteriorate at higher temperature (80°) in agreement with the earlier observations of Planner and Schlotter (*Z. Metallk.*, 1930, **22**, 41). This can be explained by the fact that with the rise in temperature, the conductivity increases due to increased mobilities of the ions, with a concomitant increment in the cathode efficiency up to 45° ; at higher temperatures, however, other factors, e.g. convection currents, lowering of hydrogen overvoltage, throwing power, etc., come into play as a result of which the efficiency diminishes.

No precise information is, however, available in the literature for the correlation of the cathode efficiency with the proportion of an addition agent in the electrolytic bath. We have studied this in greater details (*cf.* results in Table IV) in the case of various inorganic and organic agents, whose concentrations were varied, especially in a few cases over a wide range. Various theories attempting to explain the influence of addition agents, which are generally organic or colloidal substances, exist in the literature. The possible rôle of colloidal addition agents, in general, has been discussed in a review by Blum (*Colloid Symposium Monograph*, 1921, **5**, 300), who suggests the following factors for cases in which the addition agent has actually been found in the cathode deposits: "(1) co-discharge of colloid particles and metal ions, (2) discharge of complex ions containing the metal and the colloid, (3) adsorption of colloid upon the face of the metal deposit, or (4) mechanical inclusion in the deposit." Blum further states in regard to these various possibilities that "it is difficult from the meagre data available to suggest the relative probabilities of these processes..." However, other workers have expressed preference for one or the other of the particular views outlined above. Thus Bancroft (*Trans. Amer. Electrochem. Soc.*, 1913, **23**, 266) tacitly assumes that adsorption accounts for the inclusion of the addition agent in the deposit; Fuseya and Murata, (*ibid.*, 1926, **50**, 235) postulated the existence of complex cations formed from the metal ion and addition agent and produce evidence to show that such complex ions are doubtless formed (*cf.* also Marie and Buffat, *J. chim. phys.*, 1927, **24**, 470; Taft and Messmore, *J. Phys. Chem.*, 1931, **35**, 2585). Among the causes which normally promote the production of rough and 'treed' deposits is the presence of suspended impurities, especially, conducting particles of carbon, metal, etc. derived from the anodes. Upthegrove and Baker (*Trans. Amer. Electrochem. Soc.*, 1928, **53**, 389) have noticed that such impurities lodge themselves upon the cathode and serve as nuclei for the growth of large grained crystals or 'trees'. Much of the effect of addition agents in reducing roughness is that of counteracting the influence of suspended matter.

Our results with $\text{Al}_2(\text{SO}_4)_3$, $18\text{H}_2\text{O}$ show that the addition of this to the bath showed no marked improvement in the deposit; the cathode efficiency decreases steadily, owing to the plating out of Al along with Cd on the cathode. Inclusion of this as an addition agent in the present investigation was suggested because of its favourable effects in the deposition of Zn from zinc bath (Thompson, *Trans. Amer. Electrochem. Soc.*, 1926, **50**, 193) due to its buffer action and of nickel from a nickel bath (p_{H} about 5.6) as observed in these laboratories, possibly due to its hydrolysis, which commences at a p_{H} of about 5, and subsequent inclusion in the cathode deposit. Under the operating conditions of Cd-deposition from an acid bath (p_{H} about 3), $\text{Al}_2(\text{SO}_4)_3$, $18\text{H}_2\text{O}$, may not, it is anticipated, modify the structure of the deposit as its hydrolysis is arrested by the high acidity of the medium, an inference in close accord with our findings. Our results show that the addition of NiSO_4 , $7\text{H}_2\text{O}$ gives bright and smooth deposits, in agreement with the earlier observations of Westbrook (*loc. cit.*) and others, but lowers the cathode efficiency, possibly due to simultaneous deposition of Ni. The addition in traces or very little amounts of certain agents *viz.*, HgCl_2 , CrO_3 , SnCl_4 , SbCl_3 , BiCl_3 , SnO , SnO_2 , CS_2 , and pyridine gives loose, powdery, black and wholly unsatisfactory deposits. Addition of ZnSO_4 , $7\text{H}_2\text{O}$ does not show any improvement in the deposit. In presence of H_2O_2 (0.5%), the deposit gets spoiled but the cathode efficiency increases, possibly due to hydrogen evolution at the cathode being considerably arrested. A trace of SnCl_2 (0.01 %), when added to the bath, shows marked improvement in the deposit; with its increased amounts (0.1 %), a highly smooth, white, amorphous, adherent and fine-grained deposit is obtained. The cathode efficiency also increases. That SnCl_2 functions as the most efficient addition agent in Cd-deposition may, possibly, be attributed to its capacity to pass into a colloidal state, due to hydrolysis, as evidenced by a sudden but distinct development of opalescence in the solution, and its subsequent inclusion in the cathode deposit, where its presence hinders the crystal growth thus resulting in the formation of a fine-grained deposit. The presence of Sn in the cathode deposit was detected by usual qualitative tests. Addition of gelatin in small amounts to the bath gives smooth, amorphous and adherent deposit; with the increased amount the quality of the deposit gets further improved. The cathode efficiency increases with the increasing amount of gelatin, up to a certain limit (0.05%) and then diminishes with further addition. Similar results were also obtained with the addition of dextrin. Earlier results of Millian (*loc. cit.*) showed that smooth metallic deposits of cadmium are obtained with the addition of gelatin *only* from the solutions of strong acids as sulphates, fluosilicates or

fluoborates. He further states that the addition of gelatin to the acid Cd-bath renders the metallic deposit more bright and increases its hardness. Our results with the gelatin may, therefore, easily be accounted for as follows. Gelatin being a complex colloid, under the operating conditions of the bath and highly favourable acidic medium (p_H about 3, far below 4.7, the iso-electric point for gelatin) gets positively charged (Frolich, *Trans. Amer. Electrochem Soc.*, 1924, **46**, 67) and migrates on electrolysis to the cathode surface and gets included in the deposit thereby affecting the crystal structure of the deposit by minimising the grain size. The maximum values for cathodic efficiencies in the presence of 0.05% gelatin and 0.5% dextrin, may possibly be attributed to the discharge at the cathode of the complex cations of the metal with the addition agent of the type, $[Cd\ n(gelatin)]^{++}$ $[Cd\ n(dextrin)]^{++}$. Further evidence in favour of such a possibility, especially in the deposition of silver and copper, can be adduced from the earlier communications (*cf.* Joshi, Solanki and Rao, *J. Indian Chem. Soc.*, 1938, **15**, 174; Joshi and Padmanabhan, *ibid*, 1938, **15**, 185) from these laboratories. Addition of glycerine (upto 1%) and sucrose (upto 10%) to the bath, gives wholly unsatisfactory deposits (results in Table IV), possibly due to increased resistance of the bath solution.

Authors are highly indebted to Dr. S. S. Joshi for suggesting the problem and giving valuable help and criticism during this investigation.

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Received December 13, 1940.

STUDIES IN VITAMIN-C OXIDATION. PART II. INFLUENCE OF VARIOUS SUBSTANCES OCCURRING IN PLANT AND ANIMAL TISSUES ON THE CATALYTIC OXIDATION OF VITAMIN-C.

BY P. V. KRISHNAMURTHY AND K. V. GIRI.

A study has been made of the influence of various substances on the catalytic oxidation of vitamin-C by Cu . Among the substances investigated, oxalic acid, xanthine, uric acid, theophylline, creatinine, antipyrine and albumin exert powerful protective action, while tartaric, citric, malic, maleic, malonic, tannic and aspartic acids, glycine, alanine, asparagine, histamine and pyrogallol exert slight protection against the oxidation of the vitamin. Creatine, succinic acid and other compounds investigated exert no protection. The various possible mechanisms underlying the action of these substances on vitamin-C oxidation are discussed.

In a recent note (Giri and Krishnamurthy, *Nature*, 1940, **146**, 99) and in the previous part of this series (Krishnamurthy and Giri, *J. Indian Chem. Soc.*, 1941, **18**, 7) evidence was given which indicated the presence of protective factors in vegetables, which inhibit the catalytic oxidation of vitamin-C by Cu^{++} . Attempts to identify the factors were partly successful and tartaric acid was found to be present in the extract exhibiting the protective action. In addition to tartaric acid there may be many more protective constituents in plants, which have not so far been identified. The only substances, which are known to exert protective action on vitamin-C oxidation, and which also occur in plant and animal tissues, are glutathione (Hopkins and Morgan, *Biochem. J.*, 1936, **30**, 1446), cysteine, cystine, pyrophosphate (Giri, *Indian J. Med. Res.*, 1937, **26**, 443; *Z. physiol. Chem.*, 1937, **245**, 185; Krishnamurthy and Giri, *Indian J. Med. Res.*, 1941, **29**, 71), cyanide, sulphuretted hydrogen, chlorophyll and amino-acids (Ghosh, *J. Indian Chem. Soc.*, 1938, **16**, 1; Mystkowski and Lasocka, *Biochem. J.*, 1939, **33**, 1460). It was, therefore, thought that a study of the effect of various other substances, which commonly occur in plant and animal tissues, may serve to throw further light on the nature of the protective factors. The present paper deals with the influence of about sixty substances on the catalytic oxidation of vitamin-C. Several new substances have now been discovered, which exert powerful inhibiting action on the catalytic oxidation of the vitamin by Cu^{++} .

EXPERIMENTAL.

The rate of oxidation of vitamin-C was determined as described in

the previous paper (*loc. cit.*). Glass-distilled water and analytically pure chemicals were used in the experiments.

The reaction mixture contained 9 c.c. of $M/5$ -acetic acid-acetate buffer (p_H 5.6); 1 c.c. of copper sulphate solution containing 0.07 mg. of $CuSO_4 \cdot 5H_2O$, and 5 c.c. of the solution containing the substance, whose action on the oxidation of the vitamin is to be determined, were added. The total volume of the reaction mixture was made up to 20 c.c. The flasks containing the reaction mixtures were kept at 37° in an electrically controlled thermostat. After the experimental solutions attained the temperature of the thermostat, 5 c.c. of vitamin-C solution containing 5 mg. of the vitamin were added, and immediately after shaking the contents of the flask, 2 c.c. of the reaction mixture were pipetted out into a beaker containing 1 c.c. of glacial acetic acid, and titrated with the indophenol dye. The titre value, thus obtained, represents the initial value for vitamin-C. At stated intervals 2 c.c. of the reaction mixture were pipetted out and similarly titrated.

All determinations of the rates of oxidation have been made with the same amount of Cu^{++} and with the same concentration of vitamin-C. The results are, therefore, comparable, and the relative effect of the substances on vitamin-C oxidation is clearly shown.

In Table I is given the percentage of inhibition (degree of protection) exerted by each substance against the oxidation of the vitamin by Cu^{++} . The percentage of inhibition (degree of protection) is calculated according to the formula given by Giri and Shourie (*Indian J. Med. Res.*, 1940, **27**, 685).

The percentage of inhibition (degree of protection) exerted by the substance against the catalytic oxidation of vitamin-C by Cu^{++} is expressed as percentage inhibition =

$$100 \left(1 - \frac{\text{Amt. of vitamin-C destroyed in presence of the subst. in 1 hr. at } 37^\circ}{\text{Amt. of vitamin-C destroyed in absence of the subst. in 1 hr. at } 37^\circ} \right)$$

Thus, when there is complete protection without any oxidation of the vitamin, the percentage inhibition is 100.

TABLE I.

Percentage of inhibition (degree of protection) of various substances on the catalytic oxidation of vitamin-C by Cu^{++} .

Substance.	Conc. refers to the concentration of the reacting mixture.		Substance	Conc.	
	Conc	% Inhibition		Conc.	% Inhibition.
Carboxylic acids.					
Formic acid	<i>M</i> /50	0	Fumaric acid	<i>M</i> /50	11
Benzoic acid	"	0	Phthalic acid	<i>M</i> /75	0
Oxalic acid	"	82	Nicotinic acid	0.3%	0
Succinic acid	"	0	Cinnamic acid	<i>M</i> /50	0
Maleic acid	"	11			

TABLE I (contd.).

Hydroxy compounds.					
Substance.	Conc.	% Inhibition.	Substance.	Conc.	% Inhibition.
Alcohol	M/50	0	Hydroquinone	M/50	0
Glycol	"	0	Pyrogallol	"	34
Glycerol	"	0	Phloroglucinol	"	0
Phenol	"	0	α -Naphthol	0.01%	0
Catechol	"	0	β -Naphthol	0.02%	0
Resorcinol	"	0	Xanthidol	0.01%	0
Hydroxy-carboxylic acids.					
Tartaric acid	M/50	41	Malic acid	M/50	25
Citric acid	"	36	Salicylic acid	"	0
Lactic acid	"	10	Tannic acid	"	41
Malonic acid	"	23	Gallic acid	"	0
Amino compounds.					
Urea	M/50	0	Histamine	0.5%	30
Glycine	"	13	Valine	M/50	23
Creatine	"	0	Guanidine carbonate	0.5%	17
Alanine	"	20	Aspartic acid	M/50	25
Asparagine	"	36	Choline chloride	"	19
Purines.					
Xanthine	0.05%	80	Uric acid	0.0012%	75
Caffeine	0.1%	0	Theophylline	0.06%	92
Compounds having NH-CO group.					
Hippuric acid	0.2%	11	Semicarbazide hydrochloride	M/50	0
Antipyrine	M/50	83	Veronal	M/75	0
Acetanilide	"	0	Creatinine	M/50	96
Miscellaneous substances.					
Digitalis	0.5%	0	Glycogen	0.5%	0
Strophanthin	"	0	Lecithin (egg)	0.2%	31
Saponin	"	21	Fructose	M/50	0
Albumin (egg)	"	84	Peptone	0.5%	37
			Tyrosine	0.1%	1

DISCUSSION.

A significant finding of the present study is the recognition of a number of new substances, which exert powerful inhibiting action on the catalytic oxidation of vitamin-C by Cu^{++} . These substances are widely distributed in plant and animal tissues, and they are of great importance from the point of view of their relationship to the protective action of tissues on the vitamin.

Among the carboxylic acids investigated, oxalic, tartaric, citric, malonic, malic, maleic, fumaric and tannic acids exert protective action, while succinic and other acids have no effect on the oxidation. Oxalic acid exerts the greatest protection of all the acids investigated. The powerful protective action of oxalic acid against the catalytic oxidation of the vitamin possesses an interesting feature and it reveals an important function of oxalic acid in plant tissues. This finding is of great importance in view of the fact that oxalic acid occurs in the tissues of many species belonging to the higher green plants. One of the protective constituents present in *amaranth* (Krishnamurthy and Giri, *loc. cit.*) may be oxalic acid, which is known to occur in the leaves of the plant. It may be mentioned here that Watanabe (*J. Soc. Trop. Agr. Taihoku Imp. Univ.*, 1937, 8, 381; 9, 162) has already shown that oxalic acid exerts stabilising action on vitamin-C, and he has used a mixture of oxalic and metaphosphoric acid for the extraction and stabilisation of vitamin-C from vegetables. In a later communication (*ibid.*, 1937, 9, 368) he has also shown that oxalic acid retards the oxidation of vitamin-C by charcoal.

Among the hydroxy compounds, only pyrogallol exerts slight protection against the oxidation of the vitamin. It is interesting to know that hydroquinone, resorcinol and salicylic acid, which are known as antioxidants, do not exert any influence on the vitamin.

The results obtained on the influence of purines, creatinine, and creatine on vitamin-C oxidation are of great interest. The purines are with difficulty soluble in water, but the concentrations taken sufficed to exert a definite inhibiting action on the oxidation. Xanthine, uric acid and theophylline exert strong protective action against the oxidation of the vitamin (70-98% inhibition), while caffeine does not exert any influence on the vitamin.

An interesting difference between creatine and creatinine, the two important constituents of the muscle, is revealed by their influence on vitamin-C oxidation. Although creatine has no influence on the oxidation creatinine, which is the anhydride of creatine, is found to exert powerful protection against the catalytic oxidation of the vitamin.

As regards the nature of the protection exerted by some of the substances investigated, several possible mechanisms may be suggested, namely.

(1) The substance may form a complex with Cu^{++} , thereby preventing the catalytic action of the ionised Cu on vitamin-C. Citric, tartaric, oxalic and other acids may exert their action in this manner.

(2) The substance may function as hydrogen donator, thereby reducing the oxidised vitamin (dehydroascorbic acid) back to reduced vitamin, and this reduction, being much faster than the oxidation, the substance may function as a protector.

(3) The substance may form a compound with vitamin-C, which is more stable and less rapidly oxidised by Cu^{++} than the free vitamin.

However, little is known regarding the precise mechanism involved in each case. It may, however, be mentioned here that some of the substances like citric acid and the amino-acids are known to form complexes with Cu^{++} , and the protective action exerted by these substances may be attributed to this cause.

From the foregoing account it is likely that there exist certain structural chemical requirements with respect to the purines as inhibitors of vitamin-C oxidation, probably the existence of a free imino grouping in the purines *e.g.* xanthine, uric acid, and theophylline. The *N*-substituted purine caffeine does not exert any inhibition even at such a high concentration as 0.1%, while those purines, whose 7-imino-N is not substituted *e.g.*, xanthine, uric and theophylline, exert strong inhibition on the oxidation of the vitamin.

It would be premature to base any wide conclusions upon the limited findings of the work here described.

The authors wish to acknowledge with thanks the facilities granted by Major J. F. Shepherd for carrying out the above investigations in the Andhra Medical College. The authors' thanks are also due to Dr. G. Gopal Rao for discussion.

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Received November 4, 1940.

A NEW SYNTHESIS OF EUDALENE.

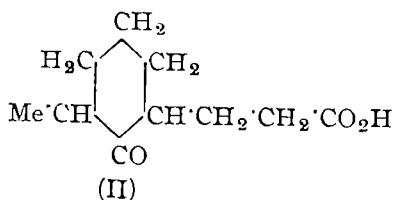
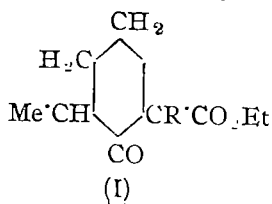
BY NRIPENDRA NATH CHATTERJEE AND AMALENDU BOSE.

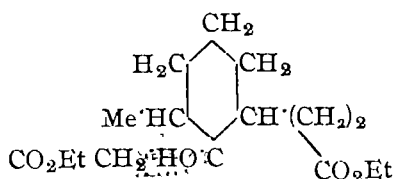
A new synthesis of eudalene has been effected starting from sodium salt of ethyl 6-methylcyclohexanone-2-carboxylate

Eudalene, obtained by selenium dehydrogenation of selenene and eudesmol, has been shown to be 1-methyl-7-isopropylnaphthalene and has been synthesised (*cf.* Ruzicka and Stöll, *Helv. Chim. Acta*, 1922, **15**, 925; Darzen and Levy, *Compt. rend.*, 1932, **194**, 2056; Barnett and Sanders, *J. Chem. Soc.*, 1933, 435).

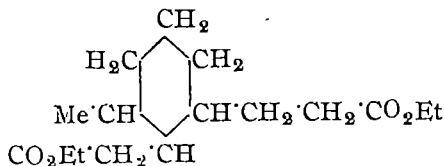
Since dicyclic sesquiterpenes are derivatives of hydrogenated naphthalenes, it was thought desirable to synthesise hydrogenated naphthalenes which will ultimately lead to the synthesis of eudalene. The following scheme describes a new synthesis of eudalene starting from cyclohexanone derivative.

Sodium salt of ethyl 6-methylcyclohexanone-2-carboxylate (I, R=H) is allowed to react with ethyl β -chloropropionate and the resulting diethyl 6-methylcyclohexanone-2-carboxylate-2- β -propionate (I, R=CH₂·CH₂·CO₂Et) is hydrolysed with hydrochloric acid to yield 6-methylcyclohexanone-2- β -propionic acid (II). Ethyl 6-methylcyclohexanone-2- β -propionate, obtained on esterification, reacts with bromoacetic ester in presence of zinc according to Reformatsky to give a mixture of diethyl 6-methylcyclohexan-1-ol-1-acetate-2- β -propionate (III) and the corresponding unsaturated ester. The crude mixture, on dehydration with thionyl chloride and pyridine in ether solution, gives a pure sample of the unsaturated ester which is then reduced in alcoholic solution by means of hydrogen in presence of platinum oxide catalyst to diethyl 6-methylcyclohexane-1-acetate-2- β -propionate (IV). The latter compound is then treated in benzene solution with molecularised sodium to yield ethyl 2-keto-8-methyldecalene-1-carboxylate (V, R=H; R=CO₂Et). On hydrolysing the above ester, 8-methyl- β -decalone (V, R=R'=H) is obtained. This when treated with isopropyl magnesium iodide according to Grignard gives a carbinol and the corresponding unsaturated compound. The mixture on selenium dehydrogenation gives eudalene (VI) identified through its picrate.

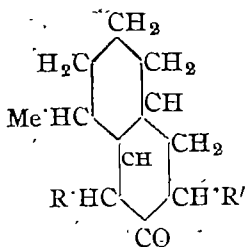




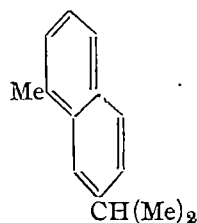
(III)



(IV)



(V)



(VI)

EXPERIMENTAL.

Ethyl 6-Methylcyclohexanone-2-carboxylate (I, R=H).—A cooled mixture of 2-methylcyclohexanone (200 g.) and ethyl oxalate (300 g.) was poured to a cold alcoholic solution of sodium ethoxide (from 40 g. sodium and 650 c.c. alcohol). The reaction mixture was allowed to stand overnight at a cool place and then decomposed by adding cold water strongly acidulated with hydrochloric acid. The ester was precipitated as a thick oil and extracted with ether. The ether extract was dried (sodium sulphate), the ether removed and the residual oil heated in vacuum. Between 95° and 100° evolution of carbon monoxide takes place. It was then heated to 180-200° in an oil-bath until the evolution of carbon monoxide was complete (about 4 hours). It was then distilled in vacuum at 97°/4 mm.

Diethyl 6-Methylcyclohexanone-2-carboxylate-2-propionate (I, R=CH₂·CH₂·CO₂Et).—(a) Finely divided metallic sodium (7.7 g.) in dry benzene (250 c.c.) was slowly treated with ethyl 6-methylcyclohexanone-2-carboxylate (60 g.) and the mixture kept overnight. Ethyl β-chloropropionate (48 g.) was then added and the mixture refluxed on a water-bath for 6 hours. It was cooled, washed with water, dried over calcium chloride and the benzene removed. The residual oil distilled at 158-65°/2.5 mm, yield 69 g.

(b) Ethyl 6-methylcyclohexanone-2-carboxylate (20 g.) was added to the solution of sodium (2.6 g.) in alcohol (31 c.c.) and the solid sodium salt

was heated under reflux for 6 hours with ethyl β -chloropropionate (18 g.). After dilution the condensation product was extracted with ether, the ether removed and the product distilled at $158-65^{\circ}/2.5$ mm., yield 21 g.

(c) A solution of sodium ethoxide from sodium (2.6 g.) in alcohol (70 c.c.) was slowly added with shaking to a mixture of ethyl 6-methylcyclohexanone-2-carboxylate (20 g.) and ethyl β -chloropropionate (16 g.), absolute alcohol (50 c.c.) and sodium iodide (0.3 g.) with cooling in a bath of ice-cold water. The reaction was allowed to proceed at room temperature for 2 hours. After refluxing for further 2 hours, the greater part of alcohol was evaporated. The residue was poured into ice-water (1 litre) and the precipitated oil isolated by means of ether. The ethereal extract was washed with water, dried and the solvent removed. It was then distilled at $158-65^{\circ}/2.5$ mm., yield 10 g. (Found: C, 63.56; H, 8.26. $C_{16}H_{24}O_5$ requires C, 63.4; H, 8.4 per cent).

6-Methylcyclohexanone-2- β -propionic Acid (II).—The foregoing ester (30 g.) was hydrolysed by refluxing with concentrated hydrochloric acid (180 c.c.) by boiling for 3-4 hours and the liquid was concentrated to a small bulk under reduced pressure and diluted with a saturated solution of ammonium sulphate. An oil then separated which was extracted with ether. The extract was dried (sodium sulphate) and evaporated. The acid was then distilled in vacuum, b.p. $165-70^{\circ}/4$ mm., which solidified on keeping in a vacuum desiccator over sulphuric acid, m.p. 71° , yield 100 g. from 120 g. of ester. (Found: C, 64.8; H, 9.0. $C_{10}H_{18}O_3$ requires C, 65.2; H, 8.7 per cent).

Ethyl 6-methylcyclohexanone-2- β -propionate was obtained by esterifying 6-methylcyclohexanone-2- β -propionic acid (70 g.) with absolute alcohol (240 c.c.) saturated with hydrochloric acid at 0° . The vessel was kept overnight at ordinary temperature. The solution was then refluxed for 4 hours. It was then cooled, treated with water and extracted with ether. The ether solution was washed with dilute solution of sodium bicarbonate, dried over calcium chloride, the ether removed and the residue distilled at $135^{\circ}/3$ mm., yield 60 g. (Found: C, 67.7; H, 9.14. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.4 per cent).

Diethyl 6-Methylcyclohexan-1-ol-1-acetate-2- β -propionate (III).—A mixture of ethyl 6-methylcyclohexanone-2- β -propionate (40 g.), bromoacetic ester (31.5 g.) and zinc wool (12.3 g.) was covered with dry benzene (150 c.c.). A crystal of iodine was added as a catalyst. On warming the mixture the reaction started and the mixture was heated for 3 hours. The solution was then decomposed with ice and sulphuric acid. Excess of zinc was filtered off and the benzene solution was washed thoroughly with ice-cold sodium carbonate

solution followed by water. After drying with calcium chloride, benzene was removed and fractionation of the residual oil gave hydroxy ester (small quantity), b.p. $167^{\circ}/3$ mm. The portion boiling below this temperature seemed to be a mixture of the hydroxy ester and the unsaturated ester. A fraction boiling at $153^{\circ}/3$ mm. gave analytical results in agreement with those of an unsaturated ester, yield 20 g. [Found (unsaturated ester) : C, 68.1; H, 8.7. $C_{16}H_{24}O_4$ requires C, 68.0; H, 9.2 per cent].

Dimethyl 6-Methylcyclohexylidene-1-acetate-2- β -propionate.—The crude hydroxy ester (82 g.) was mixed with dry pyridine (52.2 g.) and the mixture was diluted with dry ether (500 c.c.). The solution was cooled in ice and salt and thionyl chloride (34.4 g.) was added drop by drop with constant shaking. After the addition was complete, the mixture was kept at room temperature and after 2 hours, it was decomposed with ice and extracted with ether. The ethereal solution was thoroughly washed with acid and alkali. The crude solution left after evaporation of ether was diluted with benzene (300 c.c.) and heated on the water-bath with precipitated copper (5 g.) to remove sulphur. The insoluble residue was filtered, the solvent removed, and the pure oil distilled in vacuum, b.p. $153^{\circ}/3$ mm., yield 50 g. (Found : C, 68.4; H, 9.6. $C_{16}H_{24}O_4$ requires C, 68.0; H, 9.2 per cent).

Diethyl 6-Methylcyclohexane-1-acetate-2- β -propionate (IV).—The unsaturated ester (30 g.) was slowly reduced in alcoholic solution (150 c.c.) by means of hydrogen, a platinum oxide catalyst (0.5 g.) being used. The product after working up in the usual manner boiled at $149^{\circ}/3$ mm. It did not decolourise a solution of potassium permanganate. (Found : C, 67.8; H, 9.3. $C_{16}H_{28}O_4$ requires C, 67.6; H, 9.8 per cent).

Ethyl 2-Keto-8-methyldecalene-3-carboxylate (V, $R=H$: $R'=CO_2Et$ or V , $R=CO_2Et$; $R'=H$).—The foregoing ester (10 g.) and molecular sodium (1.7 g.) in dry benzene (30 c.c.) were heated on a water-bath. The heating was discontinued when the reaction became vigorous and the mixture further heated for 2 hours. After cooling, the product was treated with cold dilute sulphuric acid and the benzene layer was washed with aqueous sodium carbonate and with water, dried and evaporated. The residue in alcoholic solution gave a violet colouration with ferric chloride. The ester was obtained as a pale yellow oil, b.p. $150^{\circ}/3$ mm., yield 5 g. (Found : C, 70.4; H, 9.3. $C_{14}H_{22}O_3$ requires C, 70.6; H, 9.2 per cent).

8-Methyl- β -decalone (V, $R=R'=H$).—The keto-ester was refluxed with excess of dilute sulphuric acid (20%) for 12 hours, and the cooled solution saturated with ammonium sulphate and repeatedly extracted with ether. The extract was washed with water and dried (sodium sulphate). After

removing ether it was distilled at $101-104^{\circ}/3$ mm. (Found : C, 79.8; H, 10.9. $C_{11}H_{18}O$ requires C, 7.5; H, 10.8 per cent). The *semicarbazone* crystallised from ethyl alcohol, m.p. 177° . (Found : N, 19.3. $C_{12}H_{21}ON_3$ requires N, 18.8 per cent).

Eudalene (VI).—To an ethereal solution of isopropyl magnesium iodide (3 g., of isopropyl iodide, 10.8 g. of magnesium) was added with cooling the above ketone (3 g.) in ether. After standing for 12 hours at the ordinary temperature it was refluxed for 2 hours. The product was decomposed with ice-cold dilute hydrochloric acid. The solution was extracted with ether and the extract washed with water, dried and evaporated.

The above mixture was distilled, and the distillate mixed with three times its weight of selenium and heated for 30 hours at $300-320^{\circ}$. After cooling, the whole mass was repeatedly extracted with ether and on removal of the solvent it was distilled in vacuum. The distillate was again distilled over sodium when a clear mobile liquid was obtained having a characteristic aromatic smell.

The picrate of the hydrocarbon, prepared in the usual way, crystallised from alcohol, m.p. 92° (lit. $90-91^{\circ}$). (Found : N, 10.3. $C_{20}H_{10}O_7N$ requires N, 10.17 per cent).

Our thanks are due to Sir P. C. Ray and Prof. P. C. Mitter for their keen interest and encouragement during the progress of this work. Our thanks are also due to Mr N. Ghosh for carrying out the microanalysis of the picrate.

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Received January 21, 1941.

STUDIES IN VITAMIN-C OXIDATION. PART III, RETARDATION OF VITAMIN-C OXIDATION BY OXALIC ACID.

BY P. V. KRISHNAMURTHY.

The retardation of vitamin-C oxidation by oxalic acid has been studied in detail. It has been found that oxalic acid inhibits markedly the oxidation of vitamin-C under different conditions: (i) the uncatalysed oxidation, (ii) the oxidation catalysed by Cu^{++} and Fe^{++} , and (iii) the oxidation catalysed by the enzyme ascorbic acid oxidase. The mechanism of the inhibition is discussed.

The oxidation of vitamin-C in aqueous solution has been the subject of investigation by numerous workers. Minute quantities of Cu^{++} often present in distilled water or in reagents are sufficient to catalyse the oxidation of vitamin-C. The catalytic effect of traces of Cu^{++} is so marked that it is difficult to decide whether the autoxidation of ascorbic acid often noticed by several workers in the absence of added Cu^{++} may not be due to the presence of traces of Cu^{++} present as an impurity. Kellie and Zilva (*Biochem. J.*, 1935, **29**, 1028) found that if ascorbic acid was dissolved in pure water, distilled from quartz vessels, it was as stable as in the solid form. Barron and co-workers (*J. Biol. Chem.*, 1936, **112**, 625) found that recrystallised natural ascorbic acid dissolved in the purest water did not undergo any autoxidation upto p_H 7.6. But Ghosh (*J. Indian Chem. Soc.*, 1938, **15**, 1) reported that synthetic ascorbic acid underwent oxidation between p_H 5.8 and 7.2 in water giving a negative test for Cu^{++} with rubeanic acid or sodium diethyldithiocarbamate. McFarlane (*Biochem. J.*, 1936, **30**, 1472) found that the catalytic oxidation of ascorbic acid by Cu^{++} was inhibited by sodium diethyldithiocarbamate, cysteine and -cystine. The inhibition of vitamin-C oxidation by sulphhydryl compounds like glutathione and cysteine has been studied by Caro and Giani (*Z. physiol. Chem.*, 1934, **228**, 13), Hopkins and Morgan (*Biochem. J.*, 1936, **30**, 1446), Bersin, Koster and Justaz (*Z. physiol. Chem.*, 1935, **285**, 12), and Ghosh and Rakshit (*Biochem. Z.*, 1936, **289**, 15). Inhibition was also obtained by using oxidised forms of these compounds. The inhibition of the Cu^{++} catalysed oxidation of vitamin-C by pyrophosphate has been studied by Giri (*Indian J. Med. Res.*, 1937, **26**, 443; *Z. physiol. Chem.*, 1937, **245**, 185) and Krishnamurthy and Giri (*Indian J. Med. Res.*, 1941, **29**, 71).

Ascorbic acid which undergoes rapid oxidation either spontaneous or or catalysed *in vitro*, is strangely enough stable in vegetable and in animal

tissues. Thus Caro and Giani (*loc.cit.*) found that tissue pulp and aqueous, alcoholic and trichloroacetic acid extracts of tissues inhibit the oxidation of ascorbic acid *in vitro*. Mawson (*Biochem. J.*, 1935, 29, 569) also found that small amounts of animal tissue extracts prevent the aerobic oxidation of ascorbic acid. It is evident that animal tissues contain certain substances, which can inhibit the oxidation of vitamin-C. Two such substances may be glutathione and cystein. It has been shown (Krishnamurthy and Giri *J. Indian Chem. Soc.*, 1941, 18, 7) that out of as many as 26 substances, which exert inhibitory action on the oxidation of the vitamin in presence of Cu^{++} , oxalic acid appeared to be a powerful retarder. Hence the author has now studied in detail the mechanism of inhibition by oxalic acid

EXPERIMENTAL.

10 ml. of $M/5$ -acetic acid-acetate buffer ($p_H 5.6$) was kept in a conical flask, the requisite quantity of oxalic acid solution, brought to the same p_H by neutralisation with sodium carbonate solution containing 5 mg. of the vitamin, and then enough water to make up the total volume to 25 ml. were added. The mixture was shaken well and 2 ml. pipetted out and added to 1 ml. of glacial acetic acid and titrated immediately with 2 : 6-dichlorophenolindophenol. All the experiments were conducted at $37^\circ \pm 0.1$. All the solutions employed in this investigation were made up with water, twice distilled in glass vessels.

In Table I are given the results on the retardation of ascorbic acid oxidation at different concentrations in the absence of added Cu^{++} . The percentage of inhibition is calculated from the following formula.

$$\% \text{ Inhibition} = 100 \left(1 - \frac{\text{Amt. oxidised in 1 hr. with oxalic acid}}{\text{Amt. oxidised in 1 hr. without oxalic acid}} \right)$$

TABLE I.

Influence of oxalic acid on the spontaneous oxidation of vitamin-C.

Oxalic acid conc.	Percentage of vitamin-C oxidised			% Inhibition
	0 min.	30 min.	60 min.	
Nil.	0	26	44	
$2 \times 10^{-2} M.$	0	0	2	95
1×10^{-2}	0	0	2	95
1×10^{-3}	0	6	16	65
1×10^{-4}	0	18	34	26
1×10^{-5}	0	22	36	27
1×10^{-6}	0	26	42	Nil

It is evident from the above results that oxalic acid even in minute concentrations is able to protect the spontaneous oxidation in aqueous

solution of vitamin-C. These results also show that vitamin-C undergoes oxidation at p_H 5.6 even in the absence of added Cu^{++} , in agreement with the results of Ghosh (*loc. cit.*).

The results recorded in Table II show that oxalic acid can retard the oxidation of ascorbic acid even when catalysed by Cu^{++} ions. Blank experiments have shown that oxalic acid has no action on the indophenol dye under the conditions of the experiments.

It was thought that this inhibition might be due to complex formation between the oxalic acid and the copper ions. Hence in the experiments, the results where of are recorded in Table III, the concentration of oxalic acid was kept constant at $M/50$ and the concentration of Cu^{++} altered. For comparison the corresponding results without oxalic acid are also given.

TABLE II.

Influence of oxalic acid on the oxidation of vitamin-C catalysed by Cu^{++} .

Reagent: 10 ml. acetate buffer (p_H 5.6) + 5 mg. of ascorbic acid + 0.07 mg. $CuSO_4 \cdot 5H_2O$ + oxalic acid + water to make 25 ml.

Oxalic acid conc.	Percentage of vitamin-C oxidised.			% Inhibition.
	0 min.	30 min.	60 min.	
Nil	0	54	76	...
$2 \times 10^{-2} M$	0	4	8	89
1×10^{-2}	0	10	16	79
1×10^{-3}	0	33	52	33
1×10^{-4}	0	44	66	17
1×10^{-5}	0	44	66	17
1×10^{-6}	0	52	74	4

TABLE III.

Effect of variation of Cu concentration on the inhibition of vitamin-C oxidation by oxalic acid.

The reaction mixture consisted of 10 ml. of acetate buffer (p_H 5.6), 5 mg. of ascorbic acid, copper sulphate solution, $M/50$ -oxalic acid in the total volume, and water to make up 25 ml.

% Conc. of CuSO ₄ in soln.	Percentage of vitamin-C oxidised.						% Inhibition.
	Without oxalic acid.			With oxalic acid.			
	0 min.	30 min.	60 min.	0 min.	30 min.	60 min.	
Nil	0	26	44	0	0	2	95
0.28mg	0	52	76	0	4	8	89
0.82	0	62	84	0	10	22	73
1.68	0	64	86	0	18	30	65
2.52	0	64	86	0	22	34	60
3.08	0	62	84	0	22	34	59
4.20	0	62	84	0	22	36	57

The results indicate that if the concentration of Cu^{++} is increased, keeping the concentration of oxalic acid constant, the rate of oxidation of ascorbic acid increases, in other words, the inhibitory effect of oxalic acid diminishes.

In the following table are recorded the results on the influence of oxalic acid on ascorbic acid oxidation at p_{H} 7.2.

TABLE IV.

Influence of oxalic acid on ascorbic acid oxidation at p_{H} 7.2.

The reaction mixture consisted of 15 ml. of $M/15$ -phosphate buffer (p_{H} 7.2), 5 mg of ascorbic acid, 0.07 mg. of CuSO_4 , 5 H_2O , oxalic acid and water to make 25 ml.

Conc. of oxalic acid.	Percentage of vitamin-C oxidised			% Inhibition
	0 min.	30 min.	60 min.	
Nil	0	52	76	...
$2 \times 10^{-3} M$	0	32	46	39
1×10^{-3}	0	40	54	29
4×10^{-3}	0	42	56	26

A comparison of the results in Tables IV and II shows that for corresponding concentrations of oxalic acid, the retardation at p_{H} 5.6 is more than at the alkaline p_{H} 7.2.

Influence of Oxalic Acid on the Oxidation of Vitamin-C catalysed by Fe^{++}

The results in the following table show that Fe^{++} ions exert, though to a limited extent, some catalytic effect on the oxidation of the vitamin in aqueous solution at p_{H} 5.6 and that oxalic acid retards the catalysed oxidation.

TABLE V.

The reaction mixture consisted of 10 ml. of $M/5$ -acetate buffer (p_{H} 5.6), 5 mg. of ascorbic acid, 0.7 mg. of FeSO_4 , 7 H_2O , oxalic acid, and water to make 25 ml.

Conc. of oxalic acid.	Percentage of vitamin-C oxidised.			% Inhibition.
	0 min.	30 min.	60 min.	
Nil	0	38	56	...
$2 \times 10^{-3} M$	0	8	14	75
1×10^{-3}	0	10	20	64
4×10^{-3}	0	14	24	57
2×10^{-3}	0	16	26	53

Influence of Oxalic Acid on the Enzymic Oxidation of Ascorbic Acid.

Tauber (*J. Biol. Chem.*, 1935, **110**, 211) isolated from the pericarp of Hubbard squash an enzyme, ascorbic acid oxidase, which rapidly oxidised vitamin-C in aqueous solution. The presence of a similar enzyme has been reported in vegetables by numerous workers, notably Srinivasan (*Current Sci.*, 1935, **4**, 407), Chakrabarty and Guha (*Indian J. Med. Res.*, 1937, **24**, 839). The enzyme has been found to be highly specific for ascorbic acid. Recently Krishnamurthy and Giri (*loc. cit.*) found that pyrophosphate (which is found to inhibit the Cu^{++} catalysed oxidation of ascorbic acid) has little influence on the enzymic oxidation.

It will be of considerable interest to study the influence of oxalic acid on the oxidation of the vitamin, catalysed by the enzyme. Hence in the following experiments such a study has been made using an enzyme preparation obtained from *Cucumis sativus* according to the method described in Part I of this series.

In the following table are given the results of the influence of varying concentrations of oxalic acid on the vitamin-C oxidation with a constant concentration of the enzyme solution.

TABLE VI.

Influence of oxalic acid on the enzymic oxidation of vitamin-C.

The reaction mixture consisted of 10 ml. of acetate buffer (pH 5.6), 5 mg. of ascorbic acid, 1 ml. enzyme solution, oxalic acid and water to make up 25 ml

Conc of oxalic acid.	Percentage of vitamin-C oxidised.			% Inhibition.
	0 min.	30 min.	60 min.	
Nil,	0	68	58	...
$4 \times 10^{-3} M$	0	26	36	63
2×10^{-3}	0	42	70	29
1×10^{-3}	0	56	88	10
4×10^{-2}	0	58	92	6

A comparison of the results in Tables VI and II show that the same concentration of oxalic acid retards the enzymatic oxidation to a smaller extent than that of Cu^{++} catalysed oxidation. For instance, a concentration of $1 \times 10^{-2} M$ oxalic acid retards the enzymatic oxidation to the extent of only 10 %, while it retards the Cu^{++} -catalysed reaction to the extent

of 79%. It is to be noted, however, that even with the enzymic oxidation increased retardation is obtained at higher concentrations of oxalic acid.

In the following table are recorded the results of experiments in which the enzyme concentration was varied while the oxalic acid concentration was kept constant.

TABLE VII.

Effect of variation of enzyme concentration on the inhibition of enzymatic oxidation of vitamin-C by Cu^{++} .

The reaction mixture consisted of 10 ml. of acetate buffer (pH 5.6), 5 mg. of ascorbic acid, enzyme solution, oxalic acid to make to a total concentration of $M/50$, and water to make up 25 ml.

Enzyme solution.	Percentage of vitamin-C oxidised.		
	0 min.	30 min.	60 min.
Nil	0	0	2
1.0 ml,	0	42	70
0.75	0	44	68
0.50	0	40	62
0.25	0	24	40
0.10	0	18	28

The results indicate that the inhibition by given concentration of oxalic acid is more pronounced at lower concentrations of the enzyme than at the higher. It is possible that oxalic acid retards by forming a complex with the enzyme also.

DISCUSSION.

The results presented in this paper show that oxalic acid can markedly retard the oxidation of ascorbic acid under different conditions, namely (1) the uncatalysed oxidation, (2) the oxidation catalysed by Cu^{++} and Fe^{++} ions, and (3) the oxidation catalysed by the enzyme ascorbic acid oxidase. The inhibition is manifest even at such low concentrations as $1 \times 10^{-6} M$, while $2 \times 10^{-2} M$ concentration of oxalic acid affords almost complete protection for the Cu^{++} -catalysed reaction. Oxalic acid affords a certain measure of protection of the vitamin even against enzymic oxidation. The presence of oxalic acid and other acids like tartaric, citric, etc. which have also been found (reported in Part II of this series) to markedly inhibit the

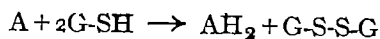
oxidation of the vitamin, explains the stability of the vitamin in several plant tissues.

Fujita and Iwatake (*Biochem. Z.*, 1935, **275**, 291) proposed the addition of metaphosphoric acid to the liquid used in extracting the vitamin from plant tissues in order to prevent its oxidation and to ensure more reliable results. Giri (*loc. cit.*) proposed the use of pyrophosphate for a similar purpose. Now the results recorded in this paper show that the degree of retardation produced by oxalic acid is much higher than that produced either by metaphosphoric acid or sodium pyrophosphate at corresponding concentrations. The addition of oxalic acid to the extracting fluid should, therefore, ensure more reliable results in the estimation of vitamin-C in plant and animal tissues. Moreover, the use of oxalic acid should prove more economical, as the cost of phosphoric acid and pyrophosphate is high.

It will be of interest to study the mechanism of this retardation produced by oxalic acid. In Part II of this series it has been suggested by us that an inhibitor may work by three alternative mechanisms.

- (1) It may form a complex with the catalyst,
- (2) It may form a more stable compound with the substrate namely ascorbic acid.
- (3) It may act as a hydrogen donator capable of reducing the oxidised form of the vitamin back to the original form.

Hopkins and Morgan (*Biochem. J.*, 1936, **30**, 1446) found that glutathione markedly inhibits the oxidation of ascorbic acid. They explained the inhibitory action of glutathione as being due to its capacity to reduce dehydroascorbic acid to ascorbic acid.



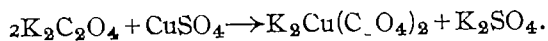
Dehydroascorbic acid.

Oxidised glutathione.

This suggestion is confirmed by the work of Borsook and Jeffries (*Science*, 1936, **83**, 397) who found that the reduced form of glutathione can actually reduce dehydroascorbic acid to ascorbic acid.

The author made experiments to see if oxalic acid can reduce dehydroascorbic acid, with negative results. Hence mechanism (3) is not possible in this case. The bulk of the evidence adduced in this paper shows that very likely oxalic acid acts by forming a complex with the catalyst, the Cu^{++} , Fe^{++} , or the enzyme, though it should be noted here that inhibition was obtained even for the uncatalysed oxidation. It is well known that

oxalic acid and oxalates form complex salts with Cu^{++} and Fe^{++} , as for instance



The concentration of oxalic acid used in each of the experiments is enough to form the complex with Cu^{++} or Fe^{++} , and the concentration of oxalic acid does not appear to decrease during the reaction.

Further work is in progress.

The author acknowledges with thanks facilities granted by Major J. F. Shepherd, Principal of the Andhra Medical College, Vizagapatam, and the help given and interest shown by Dr. G. Gopal Rao and Dr. K. V. Giri in this investigation.

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Received December 20, 1940.

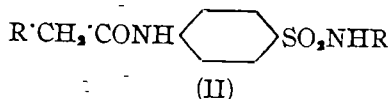
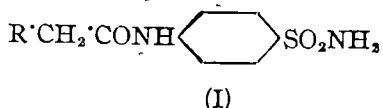


SULPHONAMIDES. PART II.

BY K. N. GAIND, R. P. SEHGAL AND J. N. RAY.

Anilino-, toluidino-, anisidino-, phenetidino-, xyloidino-, 5-aminoquinolino-, anisidino-acetylamino-*p*-benzenesulphonamides and various allied products have been synthesised for studying their therapeutic activity and toxicity

In Part I of this series of papers (*J. Indian Chem. Soc.*, 1940, **17**, 495) sulphonamides having quinoline ring in the molecule have been described. In the present investigation, sulphonamides of the type (I) and (II) have been synthesised.



where R = PhNH, EtO·C₆H₄NH, MeO·C₆H₄NH and Me·C₆H₄NH.

For this purpose, *p*-*o*-chloroacetaminobenzenesulphonyl chloride was converted into the corresponding amide, which was then condensed with various amines to give the substances of the type (I). The substances of the type (II) were obtained by direct condensation of *p*-*o*-chloroacetaminobenzenesulphonyl chloride with two molecules of the bases.

The products will be tested for their therapeutic activity and toxicity when facilities are available.

EXPERIMENTAL.

ω-Anilinoacetylamino-*p*-benzenesulphonamide (I, R = PhNH).—A solution of *p*-*o*-chloroacetylaminobenzenesulphonamide (2 g.) and aniline (2 mol, 1·5 c.c.) in absolute methyl alcohol (40 c.c.) was heated on a steam-bath for 14 hours. Alcohol was distilled off and the residue was crystallised from 33% alcohol, m.p. 196°, yield 2 g. (Found : N, 13·75. C₁₄H₁₆O₃N₃S requires N, 13·77 per cent).

The compounds described below were prepared in the same manner as the aniline derivative.

ω-Diethylaminoacetylaminobenzene-*p*-sulphonamide (I, R = NEt₂) crystallised from water, m.p. 153°. (Found: N, 14.67. C₁₈H₁₉O₃N₃S requires N, 14.7 per cent).

ω-*o*-Anisidinoacetylaminobenzene-*p*-sulphonamide.—After distilling off the methyl alcohol, the residue was extracted with boiling water, which on cooling deposited a white solid, which after crystallisation from 98% alcohol had m.p. 189°. (Found: N, 12.34. C₁₈H₁₇O₄N₃S requires N, 12.53 per cent).

ω-*m*-Anisidinoacetylaminobenzene-*p*-sulphonamide crystallised from 50% methyl alcohol, m.p. 155°. (Found: N, 12.25; S, 9.6. C₁₈H₁₇O₄N₃S requires N, 12.53; S, 9.5 per cent).

ω-*p*-Anisidinoacetylaminobenzene-*p*-sulphonamide crystallised from absolute methyl alcohol, m.p. 189°. (Found: N, 12.8. C₁₈H₁₇O₄N₃S requires N, 12.53 per cent).

ω-*o*-Toluidinoacetylaminobenzenesulphonamide (I, R = Me·C₆H₄NH).—After distilling off the methyl alcohol, the semi-solid residue was triturated with water and filtered. The residue after crystallisation from alcohol separated as rhombic plates, m.p. 212°. (Found: N, 12.96. C₁₈H₁₇O₃N₃S requires N, 13.17 per cent).

ω-*m*-Toluidinoacetylaminobenzene-*p*-sulphonamide crystallised from 70% alcohol, m.p. 166°. (Found: N, 12.81. C₁₈H₁₇O₃N₃S requires N, 13.17 per cent).

ω-*p*-Toluidinoacetylaminobenzenesulphonamide crystallised from absolute alcohol, m.p. 189°. (Found: N, 13.06. C₁₈H₁₇O₃N₃S requires N, 13.17 per cent).

ω-*o*-Phenetidinoacetylaminobenzenesulphonamide (I, R = OEt·C₆H₄NH).—A solution of *p*-*ω*-chloroacetylaminobenzenesulphonamide (1 mol., 2.5 g.) and *o*-phenetidine (2 mol., 2.7 g.) in absolute methyl alcohol (40 c.c.) was refluxed on a steam-bath for 14 hours. After cooling, the solvent was filtered off and the residue refluxed again with 40 c.c. of absolute methyl alcohol. It was then filtered hot and the insoluble residue was crystallised from dioxan in plates, m.p. 221°. (Found: N, 11.51. C₁₈H₁₉O₄N₃S requires N, 12.03 per cent).

ω-*m*-Phenetidinoacetylaminobenzenesulphonamide.—After distillation of methyl alcohol, the residue was lixiviated with cold water and then crystallised from hot water. Finally it was crystallised from 98% alcohol and had m.p. 173°. (Found: N, 11.74. C₁₈H₁₉O₄N₃S requires N, 12.03 per cent).

ω-*p*-Phenetidinoacetylaminobenzene-*p*-sulphonamide.—After the reaction the separated solids were well washed with methyl alcohol and finally

crystallised from 98% alcohol, m.p. 209° (decomp.). (Found : N, 11.84; S, 9.1. $C_{16}H_{19}O_4N_3S$ requires N, 12.03; S, 8.4 per cent).

o-*o*-Xylidinoacetylaminobenzenesulphonamide (I, R = $Me_2C_6H_3NH$).—The residue after distilling off methyl alcohol was triturated with cold water and filtered. The insoluble mass was then extracted with hot water several times. The hot water extracts, on cooling, deposited crystals, which on recrystallisation from 50% alcohol had m.p. 163° . (Found : N, 12.93. $C_{16}H_{19}O_3N_3S$ requires N, 12.61 per cent).

o-*p*-Aminoazobenzeneacetylbenzenesulphonamide (I, R = $NHC_6H_4N : NPh$)—*p*-*o*-Chloroacetylaminobenzenesulphonamide (1 mol., 1.5 g.) and *p*-aminoazobenzene (2 mol., 2.3 g.) were dissolved in absolute methyl alcohol (40 c.c.), and the mixture heated at 100° for 10 hours. The separated solids were collected and washed thoroughly with absolute methyl alcohol. The residue was crystallised from amyl alcohol in small needles, m.p. 261° (decomp.). (Found : N, 16.89. $C_{20}H_{19}O_3N_3S$ requires N, 17.11 per cent).

o-5 Aminoquinolinoacetylaminobenzenesulphonamide (I, R = C_6H_4N).—*p*-*o*-Chloroacetylaminobenzenesulphonamide (3 g.) and 5-aminoquinoline (1.5 g.) were suspended in amyl alcohol and the mixture refluxed at 140° for 6 hours. The separated hydrochloride of the product was collected, washed with a little water and then crystallised from 98% alcohol, m.p. 236° . (Found : N, 13.46. $C_{18}H_{16}O_3N_4S$, HCl requires N, 13.81 per cent).

Condensation of p-o-Chloroacetylaminobenzenesulphonyl Chloride with Aniline (II, R = NHC_6H_5).—A solution of *p*-*o*-chlorobenzenesulphonyl chloride (1 mol., 2.7 g.) and freshly distilled aniline (4 mol., 3.7 g.) in chloroform (40 c.c.) was refluxed on steam-bath for 7 hours. Chloroform was filtered off and the residue washed several times with fresh chloroform. The solvent was recovered from the combined filtrate and the washings and the residue was first washed with hot water and then with 90% methyl alcohol and finally crystallised from 98% alcohol in small needles, m.p. 202° . (Found : N, 10.99; S, 8.8. $C_{20}H_{19}O_3N_3S$ requires N, 11.02; S, 8.4 per cent).

Condensation of p-o-Chloroacetylaminobenzenesulphonyl Chloride with Diethylamine (II, R = Et_2N).—After distilling off the chloroform from the combined filtrates, the residue was extracted with ether, and the residue from ether was crystallised from 50% alcohol, m.p. 77° . (Found : N, 12.41. $C_{18}H_{21}O_3N_3S$ requires N, 12.31 per cent).

Condensation of p-o-Chloroacetylaminobenzenesulphonyl Chloride with o-Toluidine (II, R = $Me \cdot C_6H_4NH$).—The residue from chloroform was extracted with hot benzene and crystallised from 70% alcohol in plates, m.p. 170° . (Found : N, 10.18. $C_{22}H_{23}O_3N_3S$ requires N, 10.26 per cent).

Condensation of p- ω -Chloroacetylaminobenzenesulphonyl Chloride with m-Toluidine (II, R=Me·C₆H₄NH).—The residue from the chloroform filtrate was triturated with ether. The insoluble residue was lixiviated with water and filtered. The insoluble portion was repeatedly crystallised from 70% alcohol when it had m.p. 188° (decomp.). (Found: N, 10.22. C₂₂H₂₃O₃N₃S requires N, 10.26 per cent).

Condensation with p-Toluidine.—The residue from the chloroform filtrate was triturated with 90% alcohol and filtered. The residual solids were then washed with boiling 98% alcohol and then crystallised from dioxan, m.p. 296°. (Found: N, 9.88. C₂₂H₂₃O₃N₃S requires N, 10.26 per cent).

Condensation with p-Anisidine (II, R=OMe C₆H₄NH).—A solution of ω -chloroacetyl-amino-*p*-benzenesulphonyl chloride (1 mol., 2.7 g.) and *p*-anisidine (4 mol., 4.9 g.) in dry benzene (100 c.c.) was refluxed on a water-bath for 5 hours. It was filtered hot, when on cooling a crystalline product separated out which was collected and fractionally crystallised from benzene. The first crop which came out as fine needles had m.p. 185°. (Found: N, 9.62. C₂₂H₂₃O₃N₃S requires N, 9.52 per cent).

UNIVERSITY CHEMICAL LABORATORIES,
LAHORE.

Received February 10, 1941.

NEW METHOD OF SYNTHESIS OF ISOQUINOLINE DERIVATIVES.

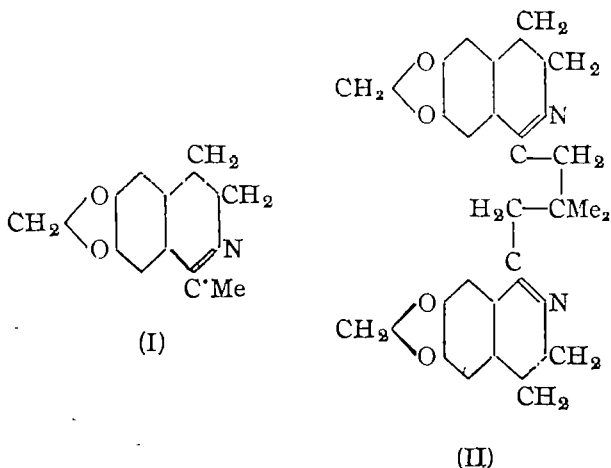
BY K. N. GAIND, (MISS) S. KAPOOR AND J. N. RAY.

In continuation of the work of Ray and co-workers (*J. Chem. Soc.*, 1932, 2510) it has been found now that the Me group of 1-methylnorhydrastinine is reactive to aldehydes and ketones other than nitro-aldehydes, under proper conditions.

Ray and co workers (*J. Chem. Soc.*, 1932, 2510) tried to prepare homologues of papavarine by condensing 1-methylnorhydrastinine (I) with different aldehydes, but the reaction failed in most cases, only *o*-nitro-benzaldehyde reacting satisfactorily.

This method, if fully established, would give an easy method of preparing isoquinolines. The conditions for the successful application of the method have now been found. In the present work an excellent yield of the important isoquinoline (I) was obtained by performing the Beckmann's transformation on the oxime of piperonylacetone, and this isoquinoline has now been successfully condensed with (i) piperonal, (ii) veratric aldehyde, (iii) anisaldehyde, (iv) propionic aldehyde, (v) acetone, (vi) acetaldehyde and (vii) cotarnine—showing that under proper conditions the Me group in (I) is reactive to aldehydes other than nitro-aldehydes (*cf.* Ray, *loc. cit.*).

In these condensations it has been found that one molecule of aliphatic aldehydes and the ketones condensed with two molecules of the isoquino-



line, but in the case of the aromatic aldehydes etc. the condensation takes place with one molecule.

It will be seen that a new general method has been worked out for lengthening the chain at position 1 or for introducing various substituents in this position. It may be mentioned that Child and Pyman (*J. Chem. Soc.*, 1931, 37; 1929, 2070) found difficulty in synthesising di-isoquinolines analogous to emetine, but the present compounds of the type (II) have the principal skeleton of the emetine structure.

It is intended to study the amœbicidal properties of these compounds as soon as opportunity offers.

EXPERIMENTAL.

Preparation of Piperonylacetone.—Piperonylideneacetone (2 g.) was reduced by hydrogen under slight pressure in ethyl acetate (150 c.c.) and absolute alcohol (30 c.c.) with 10 c.c. of 1 % palladium chloride. The reddish brown oil, obtained after distilling the solvent in *vacuo*, was crystallised from petroleum ether, m.p. 55°. The semicarbazone crystallised from alcohol, m.p. 166°. (Found: N, 16.73. $C_{12}H_{16}O_3N_3$ requires N, 16.80 per cent).

The reduced product was converted into oxime, which was crystallised from dilute alcohol, m.p. 100°, yield 3.5 g.

Preparation of the isoQuinoline from the above Oxime.—To a solution of the oxime (2.2 g.) in dry toluene (20 c.c.), was added freshly distilled phosphorus oxychloride (8 c.c.) in small quantities at a time. The mixture was gently refluxed at 130–140° for 2 hours. After cooling it was decomposed with hydrochloric acid. The acid layer was rendered strongly alkaline with sodium hydroxide and the isoquinoline extracted with ether. From the ethereal layer, dried over anhydrous sodium sulphate, the solvent was removed and the residue was crystallised from petroleum ether, m.p. 92°, yield 1.2 g.; picrate, m.p. 232° (*cf.* Decker, Kropp, Hoyer and Becker, *Annalen*, 1913, 396, 137). This method of preparing methylnorhydrastinine gives better yield than the older method (*loc. cit.*).

Condensation of Methylnorhydrastinine with Piperonal.—To a solution of methylnorhydrastinine (0.4 g.), dissolved in alcohol (10 c.c.), well powdered piperonal (1 mol., 0.38 g.) and 4 drops of piperidine were added, and the mixture refluxed on a water-bath for 4 hours. After cooling

the product was poured into very dilute hydrochloric acid, boiled and filtered. The filtrate was first extracted with ether, and then basified, avoiding rise of temperature. A sticky precipitate was obtained, which was converted into its picrate in the usual manner in absolute alcohol, and was crystallised from acetone, m.p. 156° . (Found : C, 54.1 ; H, 3.2 ; N, 10.74. $C_{25}H_{18}O_{11}N_4$ requires C, 54.54 ; H, 3.27 ; N, 10.2 per cent).

Condensation of Methylnorhydrastinine with Veratric Aldehyde.—The isoquinoline (0.6 g.) was condensed with veratric aldehyde (1 mol., 0.58 g.) in the manner described above. The condensation product was converted into picrate, which after crystallisation from alcohol, had m.p. 126° (decomp.). (Found : N, 10.35. $C_{26}H_{22}O_{11}N_4$ requires N, 9.9 per cent).

Condensation with Anisaldehyde.—A solution of the isoquinoline (1 g.) in absolute alcohol (20 c.c.) was boiled for 4 hours on the water-bath after the addition of 0.95 c.c. (1 mol.) of anisaldehyde and 7 drops of piperidine. The product was isolated as in the previous cases, and was converted into the picrate, which was several times triturated with absolute alcohol, and then crystallised from acetone, m.p. 192° (decomp.). (Found : N, 10.1. $C_{26}H_{20}O_{10}N_4$ requires N, 10.4 per cent).

Condensation with Propionic Aldehyde.—The isoquinoline (1 g.) and the aldehyde (2 c.c.) were condensed by the method described above. The picrate after crystallisation from acetone had m.p. 223° . (Found : C, 51.15 ; H, 3.97 ; N, 12.7. $C_{37}H_{32}O_{18}N_8$ requires C, 50.7 ; H, 3.6 ; N, 12.78 per cent).

Condensation with Acetone.—To a solution of isoquinoline (1.5 g.) in alcohol (25 c.c.), 5 c.c. of acetone and 2 g. of anhydrous zinc chloride were added and the mixture refluxed on a water-bath for 8 hours. The contents were filtered and alcohol was distilled off from the filtrate. The brownish semi-solid residue was suspended in water and made alkaline with sodium hydroxide solution and extracted with ether. The dark brown residue from the ethereal extract, dried over anhydrous sodium sulphate, was converted into picrate, which was crystallised from acetone, m.p. 180° . (Found : C, 50.6 ; H, 4.2 ; N, 12.34. $C_{31}H_{20}O_{11}N_8$ requires C, 50.68 ; H, 3.65 ; N, 12.7 per cent).

Condensation with Acetaldehyde.—To a solution of isoquinoline (1.5 g.) in alcohol (25 c.c.) freshly distilled acetaldehyde (10 c.c.) and piperidine (10 drops) were added and the mixture heated on a water-bath for 8 hours. The product was isolated in the usual manner, and then converted into the picrate, which on crystallisation from acetone had m.p. 172° (decomp.).

(Found : C, 49.97 ; H, 3.7 ; N, 12.49. $C_{36}H_{30}O_{18}N_8$ requires C, 50.10 ; H, 3.4 ; N, 12.90 per cent).

Condensation with Cotarnine.—Methylnorhydrastinine (1.5 g.) was dissolved in alcohol (30 c.c.) and cotarnine (1 mol., 1.9 g.) and piperidine (10 drops) were added to this solution. The mixture was refluxed on a water-bath for 5-6 hours. After cooling, it was poured into dilute hydrochloric acid, and extracted with ethyl acetate. The acid layer was made strongly alkaline and again extracted with ethyl acetate. The extract was dried over anhydrous sodium sulphate, and the solvent distilled off. The sticky residue, thus obtained, was converted into picrate, which after crystallisation from acetone had m.p. 237°. (Found : C, 50.05 ; H, 4.01 ; N, 13.37. $C_{35}H_{30}O_{19}N_8$ requires C, 49.7 ; H, 3.7 ; N, 12.97 per cent).

UNIVERSITY CHEMICAL LABORATORIES,
LAHORE.

Received February 10, 1941.

COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART II. NICKEL BIGUANIDINES.

BY PRIYADARANJAN RÂY AND BHUPESH CHANDRA PURAKAYASTHA.

Nickel bisbiguanide dihydrate, which was also isolated by earlier workers, has been prepared and found to behave as a diacidic base in all its compounds. This has been found to lose water at 110° and form the anhydrous base $\text{Ni}(\text{C}_2\text{N}_5\text{H}_8)_2$. Like the corresponding chromium, cobalt and copper compounds, previously described, it also forms a special type of inner metallic complex of the second order

A series of salts of the base with simple and complex anions, including polyiodides, has been prepared and their properties studied. These are, namely, chloride, bromide iodide, fluoride, double acid fluoride, chlorate, bromate, iodate, periodate; perchlorate, permanganate, borofluoride, nitrate, nitrite, sulphite, thiosulphate, dithionate, thiocyanate, selenate, chromate, carbonate, ferrocyanide, ferricyanide, nitroprusside, cobalticyanide, cobaltinitrite, mercuri-iodide, iodo-tri-iodide and chloro-tri-iodide. They resemble the corresponding copper compounds in many respects.

In Part I of this series a study of the preparation and properties of copper biguanidine and its various salts has been reported (Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617). References to the earlier work on complex compounds of biguanide and its substitution products with bivalent metals like copper, nickel and cobalt have also been given there. A complete discussion on the constitution of these compounds will be found in a previous paper by one of us (Rây and Saha, *ibid.*, 1937, **14**, 670). A study of the preparation and properties of the corresponding nickel biguanidine and its salts forms the subject of the present communication.

Of the various compounds studied, the hydrated base and the sulphate were described by earlier workers (*cf.* Friedrich, *Monatsh*, 1883, **4**, 888 ; Stumpf, "Dissertation", Berlin, 1934, p. 48).

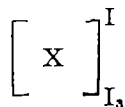
It has been observed that the salts of the base with bivalent simple anions are practically insoluble or sparingly soluble, whereas those with simple monovalent anions are generally soluble in water, the case of acid double fluoride, nitrate, iodate and periodate being exceptional. The last one has, however, behaved as a tribasic acid in the compound isolated. It has been further observed that no derivatives with mixed acid anions are formed in the case of simple univalent or bivalent anions.

Among the salts of the complex acids studied, none with mixed anions were found to be formed with dibasic and tetrabasic acids. But in the case of tri- and mono-basic complex acids, two series of salts, the normal and the

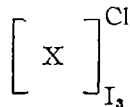
mixed, were obtained. The complex base also forms aurichloride and sparingly soluble platinichloride resembling those of organic bases.

It may further be mentioned that similarity in properties, as regards solubility and water of crystallisation, has been observed in the following groups of salts:—sulphate, chromate and selenate; nitrate and chlorate; ferricyanide and cobalticyanide. Perchlorate, permanganate and borofluoride have been found to be anhydrous and of the same crystalline shape. Besides, the nickel biguanide complexes closely resemble the corresponding copper compounds in solubility and often in containing the same number of water molecules in the crystal. These facts are in perfect accord with the isomorphous relations known among the members of each group and suggest similar relationship between the corresponding nickel and copper biguanide compounds.

The polyiodide of the complex base also presents an interesting case. Ephraim (*Ber.*, 1921, **54**, 379,394) prepared the complex polyiodide of the hexammine compounds of bivalent metals, like nickel, copper, zinc and cadmium, by the action of the corresponding complex chloride on a solution of iodine in potassium iodide. With increasing concentration of iodine he obtained higher polyiodides. But in the present case only one molecule of iodine has been found to combine with one molecule of complex nickel biguanide iodide even with a very large concentration of iodine, though, theoretically, a combination with at least two molecules might have been expected. With an excess of nickel biguanide hydrochloride, on the other hand, a chloro-polyiodide was formed, which, however, changed into the pure iodo-polyiodide when subsequently treated with an excess of potassium tri-iodide solution. Their constitutions are represented by the following formulae:



Iodo-tri-iodide



Chloro-tri-iodide

where $X = Ni (BigH^+)_2$, the nickel biguanide complex cation, $BigH$ representing one molecule of biguanide. These polyiodides in the dry state are quite stable, being unaffected by treatment with carbon disulphide. But the latter solvent can remove the whole of the excess iodine from moist polyiodide by repeated extraction. This is evidently due to the dissociation of the polyiodide ion in presence of water, though they are sparingly soluble. Their stability and low solubility might in this case be attributed to the equalisation of ionic volumes by complex formation, which renders possible a close packing to strengthen the crystal lattice.

Finally, both the dihydrate and the anhydrous base have been found to be diamagnetic, which means according to Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225), that an inner 3-*d* orbital is involved in the sharing of electrons leading to the formation of the complex (*dsp*² bonds); this gives a planar configuration of the biguanide molecules about the nickel atom.

EXPERIMENTAL.

Nickel bisBiguanidinium Chloride.—A solution of nickel chloride (1 mol.) was added, drop by drop, to a solution of biguanide sulphate (2 mols.) containing an excess of caustic soda. The crude base, mixed with a small amount of nickel hydroxide, was precipitated in the form of yellow, silky crystals. This was digested with semi-normal hydrochloric acid to give a neutral solution, which was filtered and evaporated to a small volume on the water-bath. The solution was kept overnight in the cold when a large crop of long, needle-shaped, orange-yellow crystals separated out. These were washed first with ice-cold water and then with alcohol. For analysis they were dried in air.

The chloride was also prepared by rubbing the powdered base with a concentrated solution of ammonium chloride in a mortar in the cold, when ammonia was displaced from the ammonium chloride by the complex base. {Found: N, 38.03; Cl, 19.40; Ni, 15.97. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2] \text{Cl}_{2.2}\text{H}_2\text{O}$ requires N, 38.07; Cl, 19.32; Ni, 15.96 per cent}.

Equivalent conductivity at 25°.

<i>v</i> (in litres) =	16	32	64	128	256	512	1024
λ_v	= 81.02	97.88	106.0	111.3	115.2	119.0	123.3
λ_∞ (mean) =	122.9						

From Walden's formula $\lambda_\infty = \lambda_v (1 + n_1 n_2 \cdot 0.692 v^{-\frac{1}{2}})$, where n_1 and n_2 are the valencies of the cation and the anion (*cf.* Walden, *Leitvermögen der Lösungen*, 1925, **V**, p. 33).

The mobility of $\frac{1}{2}$ Ni $(\text{C}_2\text{N}_5\text{H}_7)_2^{++} = 122.90 - 76.63 = 46.27$, the ionic mobility of the chlorine ion being 76.63 at 25° (Ferguson and Vogel, *Phil. Mag.*, 1927, *iv*, **9**, 223).

Nickel bisBiguanidinium Hydroxide.—The pure dihydrate was prepared by treating the solution of the complex chloride with that of sodium hydroxide. The silky, yellow, crystalline precipitate was filtered, washed first with water till free from alkali and then with alcohol. The crystals were dried in air free from carbon dioxide.

The substance liberates ammonia from ammonium salts, does not decompose readily when treated with alkali and sodium peroxide, and is

insoluble in organic solvents like alcohol or ether. {Found : N, 47'53 ; Ni, 19'89. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2](\text{OH})_2$ requires N, 47'50; Ni, 19'92 per cent}.

The magnetic susceptibility of the substance, measured in a Curie's balance at 27° gave $\chi_m = -0'2212 \times 10^{-6}$.

The dihydrate was also prepared by Stumpf (*op. cit.*) by treating nickel biguanide sulphate with potassium hydroxide.

Nickel bisBiguanidine.—The bisbiguanide dihydrate, when heated at 110° for about 10 hours, lost 12'3% of its weight. The calculated value for the water in the dihydrate equals 12'22 per cent. The corresponding copper compound also loses its water at the same temperature (*cf.* Rây and Bagchi, *op. cit.*). {Found : Ni, 22'80. $\text{Ni}(\text{C}_2\text{N}_5\text{H}_6)_2$ requires Ni, 22'70 per cent}.

The anhydro-base is also insoluble in organic solvents like alcohol and ether. It is reddish yellow in colour which changes to yellow on exposure to air with regeneration of the original dihydrate.

Its magnetic susceptibility at 27°, $\chi_m = -0'1491 \times 10^{-6}$.

Nickel bisbiguanidinium bromide was obtained in the form of deep yellow, crystalline precipitate by adding a strong solution of the complex chloride to that of potassium bromide. It was recrystallised from warm water and then washed and dried as described in the case of the chloride. {Found : Br, 35'48 ; Ni, 13'09. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{Br}_2 \cdot 1'5\text{H}_2\text{O}$ requires Br, 35'72 ; Ni, 13'11. per cent}.

Nickel bisbiguanidinium iodide prepared like the previous compound from the complex chloride and potassium iodide, was recrystallised from warm water and dried in air. It resembles the corresponding chloride and bromide in properties. {Found : I, 49'44 ; Ni, 11'42. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{I}_2$ requires I, 49'33 ; Ni, 11'41 per cent}.

Nickel bisbiguanidinium fluoride separated slowly as orange-yellow crystals when to a concentrated solution of ammonium fluoride, a solution of the complex chloride was added drop by drop. They were recrystallised from water, washed and dried as usual. {Found : F, 9'86 ; Ni, 15'48. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{F}_2 \cdot 4\text{H}_2\text{O}$ requires F, 10'01 ; Ni, 15'46 per cent}.

Nickel bisbiguanidinium ammonium acid fluoride was obtained as a light brown precipitate when a concentrated solution of ammonium acid fluoride was treated with that of nickel biguanide chloride. It is sparingly soluble in water. It was washed and dried as before. {Found : N, 35'18 ; F, 21'43 ; Ni, 13'37. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{F}_2 \cdot \text{HF} \cdot (\text{NH}_4)\text{HF}_2 \cdot 3'5\text{H}_2\text{O}$ requires F, 21'65 ; N, 35'10 ; Ni, 13'38 per cent}.

Nickel bisbiguanidinium chlorate was obtained from a solution of the complex chloride and that of potassium chlorate. The deep yellow crystals were recrystallised from warm water and then washed and dried as

COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS 221

usual. {Found : Cl, 16'03; Ni, 13'10. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{ClO}_2)_2 \cdot \text{H}_2\text{O}$ requires Cl, 15'93; Ni, 13'17 per cent}.

Nickel bisbiguanidinium bromate was obtained in the form of deep yellow crystals from the complex chloride and potassium bromate and was purified by recrystallisation. {Found : Ni, 10'85; BrO_3 , 47'23. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{BrO}_3)_2 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ requires Ni, 10'80; BrO_3 , 47'10 per cent}.

Nickel bisbiguanidinium iodate was obtained from a solution of the complex chloride and that of sodium iodate. The sparingly soluble, brownish yellow crystals were washed and dried as usual. {Found : Ni, 9'53; IO_3 , 56'65. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{IO}_3)_2 \cdot 0\cdot5 \text{H}_2\text{O}$ requires Ni, 9'57; IO_3 , 56'45 per cent}.

Nickel bisbiguanidinium periodate was obtained as sparingly soluble, brownish yellow crystals by treating a solution of sodium periodate with that of the complex chloride. The composition corresponds to that of a meso-periodate. {Found : Ni, 13'20; IO_5 , 31'30. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{IO}_5)_2 \cdot 7\cdot5 \text{H}_2\text{O}$ requires Ni, 13'23; IO_5 , 31'10 per cent}.

Nickel bisbiguanidinium perchlorate was prepared from a concentrated solution of sodium perchlorate and that of the complex chloride as needle-shaped, silky, yellow crystals. It was recrystallised from warm water, washed and dried as usual. {Found : Cl, 15'52; Ni, 12'75. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{ClO}_4)_2$ requires Cl, 15'45; Ni, 12'76 per cent}.

Nickel bisbiguanidinium permanganate was obtained in the form of black, shining, needle-shaped crystals by adding a dilute solution of potassium permanganate to an excess of the concentrated solution of the complex chloride. The crystals were filtered through a sintered glass crucible, washed several times with ice-cold water and then dried on a porous plate. The substance is sparingly soluble in water and takes fire when treated with concentrated sulphuric acid. {Found : Ni, 11'88; MnO_4 , 47'31. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{MnO}_4)_2$ requires Ni, 11'78; MnO_4 , 47'72 per cent}.

Nickel bisbiguanidinium borofluoride separated, on cooling a concentrated solution of the complex chloride mixed with that of ammonium borofluoride as yellow needle-shaped crystals. The crystals were filtered and recrystallised from warm water. They were then washed and dried as usual. {Found : Ni, 13'55. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{BF}_4)_2$ requires Ni, 13'52 per cent}.

Nickel bisbiguanidinium nitrate was obtained in the form of sparingly soluble, wooly, reddish brown crystals by adding a solution of the complex chloride to that of potassium nitrate. The product was purified by recrystallisation. {Found : Ni, 14'56; NO_3 , 30'70. $[\text{Ni}(\text{C}_2\text{N}_3\text{H}_7)_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ requires Ni, 14'57; NO_3 , 30'73 per cent}.

Nickel bisbiguanidinium nitrite was isolated as sparingly soluble, brownish yellow crystals by treating a solution of the complex chloride with

that of potassium nitrite. It was purified by recrystallisation from warm water. {Found : Ni, 15.81; NO₂, 24.36. [Ni(C₂N₅H₇)₂](NO₂)₂.H₂O requires Ni, 15.83; NO₂, 24.82 per cent}.

Nickel bisbiguanidinium sulphate was obtained as a yellowish brown crystalline precipitate when a concentrated solution of the complex chloride was added to that of potassium sulphate. {Found : Ni, 14.25; SO₄, 23.48. [Ni(C₂N₅H₇)₂]SO₄.3H₂O requires Ni, 14.29; SO₄, 23.37 per cent}.

The same compound was also prepared by Stumpf (*loc. cit.*) by treating a solution of biguanide acid sulphate with that of nickel sulphate dissolved in ammonia.

Nickel bisbiguanidinium sulphite separated in the form of very sparingly soluble, yellowish brown crystals when a concentrated solution of the complex chloride was added to a freshly prepared solution of sodium sulphite. {Found : Ni, 14.85; SO₃, 20.36. [Ni(C₂N₅H₇)₂]SO₃.3H₂O requires Ni, 14.87; SO₃, 20.28 per cent}.

Nickel bisbiguanidinium thiosulphate was obtained from a concentrated solution of the complex chloride and that of sodium thiosulphate. The substance forms brownish yellow crystals and is almost insoluble in water. {Found : Ni, 14.30; S₂O₃, 27.40. [Ni(C₂N₅H₇)₂]S₂O₃.2H₂O requires Ni, 14.35; S₂O₃, 27.43 per cent}.

Nickel bisbiguanidinium dithionate was prepared from a concentrated solution of the complex chloride and that of sodium dithionate. The insoluble biscuit-coloured crystalline precipitate was washed and dried as usual. {Found : Ni, 12.87; S₂O₆, 34.89. [Ni(C₂N₅H₇)₂]S₂O₆.2H₂O requires Ni, 12.85; S₂O₆, 35.01 per cent}.

Nickel bisbiguanidinium thiocyanate was obtained as golden yellow crystals, moderately soluble in water, by mixing a concentrated solution of the complex chloride with that of ammonium thiocyanate. The product was purified by recrystallisation from warm water. {Found : Ni, 15.59; SCN, 30.86. [Ni(C₂N₅H₇)₂](SCN)₂ requires Ni, 15.58; SCN, 30.82 per cent}.

Nickel bisbiguanidinium selenate was obtained as biscuit-coloured crystalline precipitate by mixing solutions of ammonium selenate and the complex chloride {Found : Ni, 12.81; SeO₄, 31.13. [Ni(C₂N₅H₇)₂]SeO₄.3H₂O requires Ni, 12.81; SeO₄, 31.27 per cent}.

Nickel bisbiguanidinium chromate was obtained in the form of yellow, insoluble crystals by treating a solution of potassium chromate with that of the complex chloride. {Found : Ni, 13.54; CrO₄, 26.86. [Ni(C₂N₅H₇)₂]CrO₄.3H₂O requires Ni, 13.62, CrO₄, 26.94 per cent}.

Nickel bisbiguanidinium carbonate was precipitated in the form of orange-yellow crystals by adding a concentrated solution of the complex

chloride to that of sodium carbonate {Found : C, 16.77 ; H, 5.10 ; Ni, 16.40. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{CO}_3 \cdot 2\text{H}_2\text{O}$ requires C, 16.82 ; H, 5.05 ; Ni, 16.46 per cent}.

Nickel bisbiguanidinium ferrocyanide was obtained as a light yellow, insoluble precipitate by adding a concentrated solution of the complex chloride to that of potassium ferrocyanide. {Found : Fe, 7.0 ; Ni, 14.47. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]_2\text{Fe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ requires Fe, 6.94 ; Ni, 14.58 per cent}.

Nickel bisbiguanidinium ferricyanide was obtained from solutions of potassium ferricyanide and the complex chloride as a deep green, sparingly soluble, crystalline precipitate. {Found : Fe, 8.56 ; Ni, 13.47. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ requires Fe, 8.50 ; Ni, 13.40 per cent}.

Nickel bisbiguanidinium nitroprusside was isolated as moderately soluble, biscuit-coloured crystals by adding a solution of the complex chloride to that of an excess of sodium nitroprusside. {Found : Fe, 11.40 ; Ni, 11.91. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2] \left[\begin{array}{c} (\text{CN})_5 \\ \text{Fe} \\ (\text{NO}) \end{array} \right] \text{H}_2\text{O}$ requires Fe, 11.29 ; Ni, 11.87 per cent}.

Nickel bisbiguanidinium cobalticyanide was obtained from a solution of potassium cobalticyanide and that of the complex chloride as brownish yellow crystals, sparingly soluble in water. {Found : Co, 8.98 ; Ni, 13.29. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]_2[\text{Co}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ requires Co, 8.93 ; Ni, 13.34 per cent}.

Nickel bisbiguanidinium cobaltinitrite was prepared like the previous compound from a concentrated solution of sodium cobaltinitrite and that of the complex chloride, when an insoluble, deep yellow, crystalline precipitate was formed. {Found : Co, 6.69 ; Ni, 9.97. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]_2[\text{Co}(\text{NO}_2)_6] \cdot 18\text{H}_2\text{O}$ requires Co, 6.64 ; Ni, 9.91 per cent}.

Nickel bisbiguanidinium mercuric iodide separated as a light yellow, crystalline precipitate, when a solution of potassium mercuric iodide was added to that of the complex chloride. {Found : I, 52.82 ; Hg, 20.88 ; Ni, 6.01. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2]\text{HgI}_4$ requires I, 52.40 ; Hg, 20.70 ; Ni, 6.06 per cent}.

The unstable HgI_4' ion, which exists only in solution in the case of potassium mercuric iodide, is here stabilised by combination with a complex cation of large volume. In the solid state potassium mercuric iodide has the composition KHgI_3 .

Nickel bisbiguanidinium Iodo-tri-iodide.—To an excess of a solution of iodine in potassium iodide, a solution of the complex chloride was added drop by drop. The brownish black, needle-shaped crystals of

the polyiodide separated out. These were filtered through a sintered glass crucible, washed several times with ice-cold water and dried on a porous plate for 4-6 hours.

The substance is difficultly soluble in water, but readily dissolves in alcohol, when freshly prepared. {Found : I (total), 63.53 ; I (associated), 32.0 ; Ni, 7.38. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2] \frac{\text{I}}{\text{I}_3} \cdot 1.5\text{H}_2\text{O}$ requires, I (total), 63.83 ; I (associated), 31.91 ; Ni, 7.38 per cent}.

Nickel bisBiguanidinium Chloro-tri-iodide.—To a solution of potassium tri-iodide a concentrated solution of the complex chloride was added, drop by drop, the brownish black crystals of the complex iodo-tri-iodide, first precipitated, turned into dark green crystals with an excess of the complex chloride. The solution with the precipitate was allowed to remain for about half an hour. The crystals were then filtered through a sintered glass crucible, washed several times with a solution of the complex chloride and then finally with cold water. They were dried as in the previous case.

The compound forms dark green, needle-shaped crystals, difficultly soluble in water and insoluble in alcohol. It is converted into the brownish black crystals of the iodo-tri-iodide with an excess of potassium tri-iodide. {Found : Cl, 4.81 ; I (total), 52.04 ; I (associated), 34.58 ; Ni, 7.99. $[\text{Ni}(\text{C}_2\text{N}_5\text{H}_7)_2] \frac{\text{Cl}}{\text{I}_3} \cdot 3\text{H}_2\text{O}$ requires Cl, 4.86 ; I (total), 52.1 ; I (associated), 34.73 ; Ni, 8.03 per cent}.

On the addition of solutions of the following salts to a solution of the complex chloride, precipitates with characteristic colours were obtained.

Potassium Bismuthi-iodide, KBiI_4 .—Crimson-coloured, crystalline product, soluble in alcohol, but readily hydrolysed by water. With excess of the complex chloride an orange yellow compound with chlorine in the anion was formed. This is insoluble in alcohol, but readily hydrolysed in water.

Potassium Chromithiocyanate, $\text{K}_3\text{Cr}(\text{SCN})_6$.—Bluish violet, insoluble precipitate. With an excess of the complex chloride the colour changes to light violet and contains chlorine in the anion.

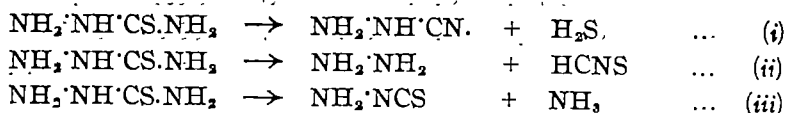
Sodium platinichloride, as well as the aurichloride, give yellow, insoluble, crystalline precipitates.

THE PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N·C·S-. PART X. ACTION OF HYDROLYTIC AGENTS, ALKALINE LEAD ACETATE, AND NITROUS ACID ON THIOSEMICARBAZIDE.

BY RAMCHANDRA SAHASRABUDHEY AND HANS KRALL.

Thiosemicarbazide on refluxing with *N*-alkali decomposes to $\text{NH}_2\cdot\text{NHCN}$ and H_2S , and with *N*-HCl very little change takes place, only small amount of it decomposes to $\text{NH}_2\cdot\text{NH}_2$ and HCNS . Alkaline lead acetate has been found to desulphurise thiosemicarbazide; from the desulphurised product a picrate of probable composition $(\text{NH}_2\cdot\text{NHCN})_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{OH}$ has been isolated. Nitrous acid has been found to transform thiosemicarbazide into amidothiotriazole.

By analogy with phenylthiocarbamide (Mehta and Krall, *J. Indian Chem. Soc.*, 1935, 12, 635) the decomposition of thiosemicarbazide is expected to proceed according to the following equations :



All these products have been found excepting thiocyanamide, which undergoes further decomposition (*Ber.*, 1896, 29, 2500); aminocyanamide could be detected only in traces in the form of a picrate, perhaps of its dipolymer.

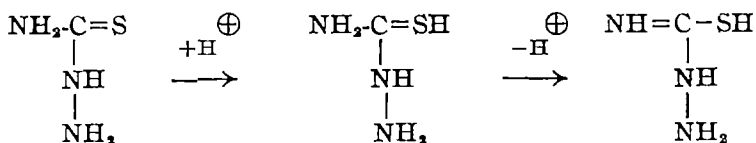
Refluxing with *N*-alkali in molecular proportions gave :

Time 1 hour. Found : HCNS , 1'44%, NH_3 , 0'48%, H_2S , 7'8%.

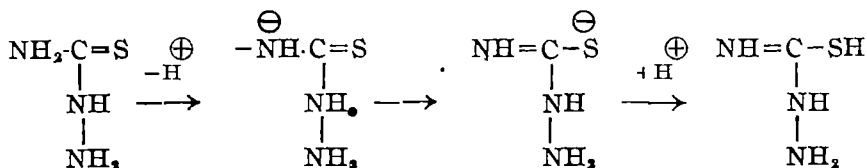
Time 4 hours. Found : HCNS , 10'5%, NH_3 , 10'2%, H_2S , 21'6%.

From these figures it is evident that the decomposition takes place predominantly according to the equation (i). The excessive formation of ammonia, with comparatively little hydrogen sulphide on prolonged heating indicates the further hydrolysis of aminocyanamide. With *N*-hydrochloric acid very little change occurs, but equation (ii) predominates. The trend of these changes, both with alkalis and acids, is similar to those with phenylthiocarbamide. The following schematic representation indicates the prototropic change involved in the tautomerism of thiosemicarbazide.

In acid medium :

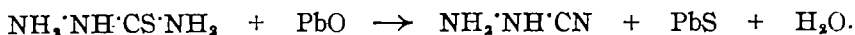


In basic medium :

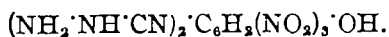


An acid medium favours the change to the pseudo form.

Action of Alkaline Lead Acetate.—Alkaline lead acetate is found to desulphurise thiosemicarbazide. Aminocyanamide is expected to be formed:

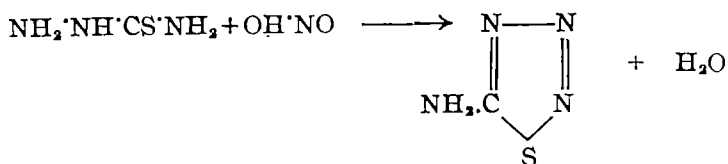


From the desulphurised product a picrate (m.p. 272°) is obtained which gives nitrogen values agreeing with the composition



Action of Nitrous Acid.—Freund and Schander (*Ber.*, 1896, 29, 2500) found that thiosemicarbazide reacted in equimolecular proportions with nitrous acid at ordinary temperatures forming amidothiotriazole.

A gasometric study of this reaction has been undertaken and it is found that practically no gas is evolved in presence of normal hydrochloric acid. Amidothiotriazole has been isolated from this mixture confirming that the reaction can be represented as



(Amidothiotriazole.)

A second equivalent of nitrous acid in presence of *N*-hydrochloric acid produces 19.2 c.c. of the gas at N. T. P. from $\frac{1}{2}$ mg. mole of thiosemicarbazide. The composition of the gas is found to be 20% NO and 80% N₂. Evidently this is only the action of nitrous acid on the amidothiotriazole first produced, indicating that it too is tautomeric and may be worth investigating.

EXPERIMENTAL.

Thiosemicarbazide was prepared by isomerising hydrazine thiocyanate (*cf. Ber.*, 1896, 29, 2501). By careful manipulation the yield was increased by about 15%, for it was found that if heating was continued after the mixture had begun to froth, signs of decomposition appeared and the yield decreased. Thiosemicarbazide with ferric salts is found to give a red colouration which is not extractible with ether.

Estimation of Thiocyanic Acid.—The hydrolysate obtained is a complicated mixture containing unchanged thiosemicarbazide with hydrogen sulphide, and thiocyanic acid in the form of their alkali salts, and hydrazine and aminocyanamide etc. The facts that (i) many of these are of a strong reducing nature; (ii) thiosemicarbazide itself gives a red colouration with ferric salts in presence of nitric acid; (iii) it also reacts under the same conditions with silver nitrate; (iv) hydrogen sulphide persists even in presence of dilute nitric acid render the estimation of thiocyanic acid difficult. The procedure finally adopted was to neutralise the alkaline solution with slight excess of dilute sulphuric acid. This removed some of the hydrogen sulphide and the remainder was removed by precipitation with freshly prepared cadmium carbonate. The filtrate was treated with dilute sulphuric acid and warmed; *m*-nitrobenzaldehyde in hot aqueous solution was then added drop by drop with constant stirring, the mixture being maintained just below the boiling point for about 5 minutes. The liquid was cooled to room temperature and filtered, thiocyanic acid being estimated in the filtrate by Volhard's method.

Estimation of Hydrogen Sulphide.—The mixture, taken in a wide test tube fitted with a cork with two delivery tubes, was decomposed with 6 *N*-sulphuric acid and a steady stream of carbon dioxide bubbled through it for 1 hour. The hydrogen sulphide was thus swept on to a zinc acetate trap containing approximately *N*/5-zinc acetate solution to which were added ammonium chloride and ammonium acetate, where it was precipitated as zinc sulphide. The precipitate, filtered and washed with a little water containing ammonium chloride and ammonium acetate, was added to an excess of standard iodine solution and decomposed with dilute hydrochloric acid, the excess of iodine being titrated with thiosulphate.

The apparatus was completely air-tight to avoid oxidation of hydrogen sulphide.

CONCLUSIONS.

1. As with phenylthiocarbamide (*J. Indian Chem. Soc.*, 1935, 12, 636) the hydrolysis of thiosemicarbazide either with acids or alkalis is of a dissociation type rather than truly hydrolytic.

2. Change No. (i) predominates in alkaline medium, while (ii) is more marked in acidic or neutral media. There is no conclusive evidence of change (iii), and if it takes place at all, it goes to a very small extent. These changes indicate that thiosemicarbazide exists predominantly in the carbamide structure $(\text{NH}_2 \cdot \text{NH} \cdot \text{C} \cdot \text{NH}_2)$ in alkaline medium, while in acid or



neutral media the predominant form is $\text{NH}_2 \cdot \text{NH} \cdot \text{C} = \text{NH}$.



3. Thiosemicarbazide is more reluctant to undergo dissociation; the extent of its decompositions is less than those of phenylthiocarbamide.

4. Thiosemicarbazide like phenylthiocarbamide undergoes desulphurisation with alkaline lead acetate. No aminocyanamide was isolated, but a picrate with the probable composition $(\text{NH}_2 \cdot \text{NH} \cdot \text{CN})_2 \cdot \text{C}_6\text{H}_5 \cdot (\text{NO}_2)_3 \cdot \text{OH}$ was obtained, m.p. 272° .

5. Nitrous acid in 1 : 1 ratio transforms thiosemicarbazide into amidodithiotriazole. In 2 : 1 ratio gases are formed, but this is evidence of tautomerism in the amidodithiotriazole first formed.

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Received January 13, 1941.

DECOMPOSITION OF POTASSIUM NITRATE IN SUNLIGHT.

By T. V. SUBBA RAO AND G. GOPALARAO.

The photodecomposition of potassium nitrate in aqueous solution has been shown to occur in sunlight filtered through pyrex glass. The results are discussed in relation to the absorption spectrum of nitrates.

It has been noticed by many investigators that potassium nitrate decomposes in dilute aqueous solution when exposed to ultraviolet light yielding potassium nitrite and oxygen. The reaction is a complex one and is influenced by a variety of factors. Warburg (*Sitzungsber. preuss. Akad. Wiss.*, 1918, 1228) found that in polychromatic ultraviolet light, the photolysis occurs more rapidly in alkaline than in neutral or acid solutions. Warburg also studied the photochemical yield of nitrite in alkaline solution in ultraviolet light of wave-lengths 2070, 2530 and 2820Å. The quantum yield was in all cases much less than unity, increasing with increasing concentration and decreasing with increasing wave-length. Warburg suggested the hypothesis of a primary dissociation of the nitrate molecule when the energy of the absorbed quantum is sufficiently large but ascribed the low quantum yields to loss of energy by "damping" during absorption, the energy being shared with solvent molecules.

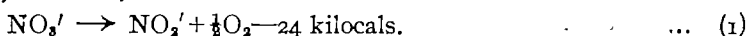
Anderson (*J. Amer. Chem. Soc.*, 1924, **46**, 797) criticised the work of Warburg and stated that the photolysis of nitrate is a reversible reaction and soon attains a photostationary state after a small amount of nitrite has been formed. Villars (*J. Amer. Chem. Soc.*, 1927, **49**, 326) denied the existence of a photostationary state and ascribed the results of Anderson to a faulty analytical method. Villars also determined the effect of hydrogen-ion concentration on the quantum yield, a variable which Warburg had indicated as existing. Using a light of wave-length of 2540Å, Villars showed that from p_H 6 to p_H 10 the quantum yield rose from 0.1 to 0.3 and was reasonably constant beyond this p_H . He also showed, in agreement with Warburg, that with increasing wave-length of light beyond 2540Å, the quantum yield at p_H 9.9 steadily fell. At 2700Å, the value was 0.07; at 3020Å, 0.013 and at 3660Å, 0.0.

The absorption spectra of nitrates have been studied by Halban, Scheibe, Morton, Maslakowicz and others ("Handbuck der Physik", 21, 329-31). For inorganic nitrates of lithium, sodium, potassium, ammonium, calcium, strontium, barium and magnesium the spectra have been studied in aqueous solutions of various concentrations. For concentrated solutions, the positions

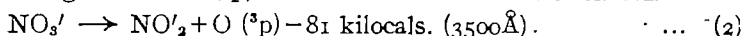
of the absorption bands and also their intensities vary with the nature of the salt and its concentration. But for dilute solutions the absorption spectra are identical for all the salts. Evidently in dilute solution, where electrolytic dissociation is fairly complete, we are dealing with the absorption of the characteristic NO_3' ion. The absorption spectrum consists of two bands separated by a region of more or less free transmission; the first band extends from about 3500\AA to 2600\AA with its maximum at about 3000\AA ; the other band, which is much more intense, begins at about 2300\AA and has its maximum at about 2000\AA . There is relatively feeble absorption beginning at about 2800\AA . Recently Krishnan and Guha (*Proc. Indian Acad. Sci.*, 1934, **8A**, 242) have ascribed the absorption bands to the photodissociation of the molecule of nitrate, following the work of Victor Henri on predissociation spectra. From the following table in which the heats of formation, in very dilute solutions, of some nitrates are listed ("International Critical Tables", Vol. 5) it will be seen that the difference between the values for the NO_3' and NO_2' ions is 101 kilojoules or 24 kilocalories and is constant for any nitrate and the corresponding nitrite.

	Na'	K'	NH_4'	Ba''
NO_3'	449.2	460.8	340.9	956.0
NO_2'	348.0	359.0	240.6	753.0
Difference	101	102	100.3	2×101.5

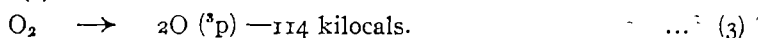
We can, therefore, write the thermochemical relation



Krishnan and Guha (*loc. cit.*) suggest that the absorption, which begins at about 3500\AA , is due to the photodissociation of the NO_3' ion to NO_2' ion and an O atom in the ground state (^3p). We therefore obtain the relation

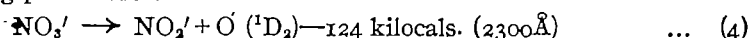


From (1) and (2) we obtain



i.e., the energy required to dissociate an oxygen molecule into two normal oxygen atoms is 114 kilocal. per gram mol. This value is in fair agreement with the values of 114.6 and 115.4 obtained by Henri from the predissociation limits of NO_2 and SO_2 molecules respectively.

The second absorption band which begins at about 2300\AA is ascribed to the following photodissociation



From the above considerations, it is possible to obtain dissociation of the potassium nitrate into nitrite in the regions of the two absorption bands. Warburg showed that photodecomposition occurs in the wave-lengths 2070\AA , 2530\AA and 2820\AA . As for the photochemical action of the second absorption band beginning at 3500\AA , the data available are meagre.

DECOMPOSITION OF POTASSIUM NITRATE IN SUNLIGHT 231

Dhar (*J. Phys. Chem.*, 1925, **29**, 926) reported slight decomposition of nitrate under the influence of sunlight.

It is felt by us that it is necessary to establish by careful investigation whether the absorption band on the long wave limit is photochemically active or not. In the present investigation we have studied, under different conditions, the decomposition of potassium nitrate in pyrex flasks exposed to sunlight in which wave-lengths shorter than 2900\AA are absent. The transmission of pyrex glass is given below as taken from International Critical Tables, II, 106.

Transmission factor (*A*) for laboratory pyrex glass.

Thickness = 1 mm.

λ	3960 \AA	3840 \AA	3610 \AA	3470 \AA	3300 \AA	3090 \AA	2800 \AA
$A = (I/I_0)$	1.00	0.97	0.93	0.85	0.70	0.50	0.05

EXPERIMENTAL.

In this investigation Kahlbaum's potassium nitrate (Analytical Reagent) was used. The various solutions were made up with water redistilled in a quartz still and stored in pyrex or Jena bottles. 40 Ml. of nitrate solutions were exposed to sunlight in pyrex conical flasks* of capacity 100 ml. and closed with corks. From time to time an aliquot portion of the solution was withdrawn and the nitrite formed by decomposition was estimated by the colorimetric method of Griess-Ilosvay. Due precautions were taken that the chemicals and water used in the course of estimation are free from nitrite as shown by the failure to respond to the Griess-Ilosvay test. The experiments were conducted in September-November.

TABLE I.

Influence of concentration.

Conc. of KNO_3 .	Nitrite-nitrogen per litre.			
	25 hrs.	50 hrs.	75 hrs.	100 hrs.
2.0M	1.21 mg.	2.24 mg.	3.85 mg	5.53 mg.
1.0	1.19	1.92	3.82	5.50
0.5	1.13	1.60	2.80	4.38
0.1	0.50	0.84	1.66	2.19
0.05	0.39	0.76	1.12	1.72
0.005	0.15	—	0.73	1.14
0.0025	0.074	—	0.42	—

* Flasks containing potassium nitrate solutions, identical to those exposed to sunlight, were kept in the dark to serve as blanks. No nitrite was detected in any of these flasks in the time intervals stated.

TABLE II.

Influence of p_H . $KNO_3 = 0.5 M.$

Conc of KNO_3 .	Nitrite nitrogen per litre			
	25 hrs	50 hrs	75 hrs	100 hrs
7.5 mol.	0.9 mg.	1.16 mg	2.08 mg	2.95 mg
7.58	1.40	2.67	3.54	3.90
8.09	1.75	3.11	5.20	6.59
8.61	2.20	3.81	5.25	6.72
9.08	2.64	4.75	7.30	8.00
10.20	2.52	3.86	6.66	7.00
10.80	4.48	6.42	11.80	13.80
11.20	6.27	9.79	16.15	22.60
11.60	8.00	14.97	28.00	36.10
12.00	11.05	18.67	28.75	50.00

From the results in Table I it is evident that the decomposition of nitrate takes place in sunlight filtered through pyrex glass; with increase in the time of exposure there is an increase in the amount of nitrite obtained. Moreover, it is seen that the rate of decomposition decreases on lowering the concentration of nitrate. From Table II it will be seen that the p_H of the solution has a profound influence on the rate of decomposition, the higher the p_H , the higher is the rate of decomposition. The p_H indicated in the table can only be approximate as the experimental solutions were kept up for many weeks without any special precautions for preventing access of carbon dioxide of the atmosphere. The experimental solution in each case was made up by adding 87.5 ml. of a buffer solution of known p_H to 12.5 ml. of 4M-potassium nitrate solution freshly prepared. For p_H 7.58 to 9.08 Sørensen's borate-hydrochloric acid mixtures (*cf.* Clarke, "Determination of Hydrogen Ion Concentration", 1928, p. 209), for p_H 10.2 to 10.8 soda-borax buffers of Kolthoff and Vlesschhouwer (p. 215) and for p_H 11.2 to 12.0 alkaline phosphate buffers of Kolthoff and Vlesschhouwer (p. 216) were employed.

It is thus clear from our results that potassium nitrate undergoes decomposition in sunlight filtered through pyrex glass. When we take into account the spectral distribution of solar radiation and the transmission of pyrex glass we can conclude that the decomposition occurs in radiation of wave-length longer than 2900\AA .

Further work is in progress.

A NEW SYNTHESIS OF CADALENE *

BY PHANINDRA CHANDRA DUTTA.

A new synthesis of cadalene has been described starting from *p*-methylacetophenone.

Since the isolation of cadalene from cadinenes, several syntheses of this substance have been recorded (Ruzicka and Seidel, *Helv. Chim. Acta*, 1922, **5**, 369; Cook and Burnett, *J. Chem. Soc.*, 1933, 22; Chatterjee, *J. Indian Chem. Soc.*, 1936, **13**, 536).

In the present investigation a new synthesis of cadalene has been described. *p*-Methylacetophenone has been condensed with chloroacetic ester according to Darzen (*Compt. rend.*, 1906, **142**, 714) to give (I) in presence of sodium ethoxide in alcohol-petroleum ether suspension (*Ber.*, 1936, **69**, 2017). Hydrolysis of the glycide ester with alcoholic solution of sodium ethoxide proceeds almost quantitatively with the addition of one molecule of water (*Ber.*, 1905, **38**, 703). When the sodium salt, thus obtained, is decomposed with ice and hydrochloric acid, there is an immediate evolution of carbon dioxide with the separation of an oil. The aldehyde, thus obtained, is purified by steam-distillation, (semicarbazone, m.p. 158°). On oxidation with silver oxide the corresponding acid has also been obtained.

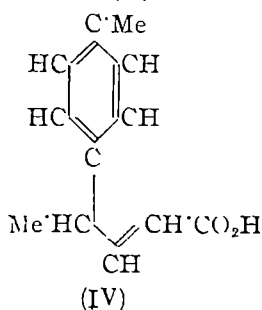
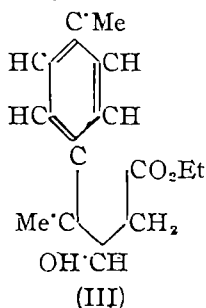
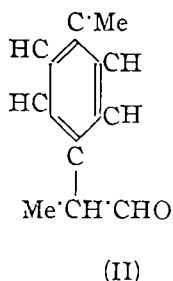
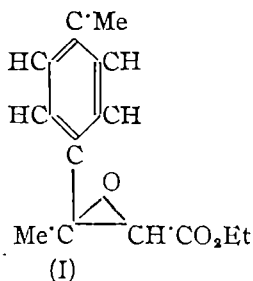
This aldehyde was first obtained by the interaction of chromyl chloride with cymene (*Ann. chim. phys.*, 1881, **v**, **22**, 259; *Compt. rend.*, 1880, **90**, 534; cf. Paterno and Schichilone, *Gazzetta*, 1880, **10**, 53). Richter and Schuchner (*Ber.*, 1884, **17**, 1931) identified it as (*p*-tolyl)-propionaldehyde by oxidation and similar reactions. Henderson and Cameron (*J. Chem. Soc.*, 1909, **96**, 973) obtained the same aldehyde by the action of chromyl chloride on terpenene. It has already been shown by Errera (*Gazzetta*, 1889, **19**, 528; 1891, **21**, 76) and by Miller and Rohde (*Ber.*, 1890, **23**, 1070; 1891, **24**, 1356), that this substance is the main product of the Etard's reaction on cymene. Limonene also yields the same aldehyde under similar conditions (cf. *J. Chem. Soc.*, 1907, **91**, 1871).

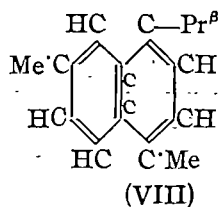
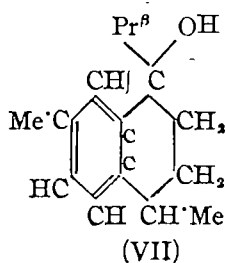
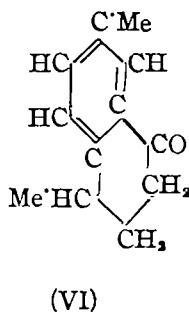
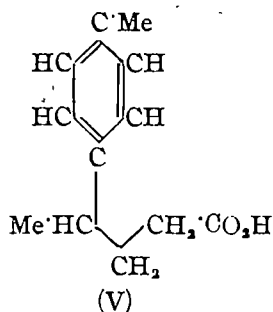
The aldehyde reacts with bromoacetic ester in presence of zinc according to Reformatsky to give (III). This on dehydration with thionyl chloride and pyridine in ether solution gives an unsaturated ester in poor yield. On distillation, the substance polymerises quickly. The most probable explanation of this appears to be the presence of the substituted phenyl group in the γ -position with respect to the carboxyl group, for the chief effect of this group is to confer an unusual degree of stability on the double

* A preliminary note appeared in *Science and Culture*, 1940, **8**, 561.

bond in the $\alpha\beta$ -position. Attempts to prepare $\alpha\beta$ -unsaturated acids by the action of bases on α -halogenated γ -phenylbutyric acids lead to unexpected results (*cf.* Linstead and Williams, *J. Chem. Soc.*, 1926, 2738; Perkin and Hope, *J. Chem. Soc.*, 1909, 95, 1360). Other dehydrating agents like phosphorus pentoxide in benzene solution and potassium bisulphate at 160° give similar results.

The aldehyde condenses smoothly with malonic acid in pyridine solution in presence of piperidine giving an acid (m.p. 85° - 86° , IV) in which the shifting of the double bond has taken place to the $\beta\gamma$ -position under the experimental conditions used and this explains its stability towards reducing agents like sodium amalgam. It is of interest to note that phenylacetaldehyde appears to be unique in yielding $\beta\gamma$ -acids under all conditions of condensation (Vorlander, *Annalen*, 1906, 345, 244). It is also significant to note that Rupe obtained (IV) directly by the action of magnesium methyl iodide on *p*-tolylpropionic ester, dehydration and hydrolysis taking place simultaneously (*Ber.*, 1911, 44, 584). Further support in favour of its $\beta\gamma$ -structure is given by the fact that it can be converted into γ -lactone by boiling with dilute sulphuric acid and this in its turn can be reduced to (V). The saturated acid smoothly undergoes cyclisation with 85% H_2SO_4 and by the action of isopropyl magnesium iodide on the ketone (VI), a mixture of (VII) and the corresponding unsaturated compound results. This mixture, on selenium dehydrogenation gives cadalene (VII), identified through its picrate.





E X P E R I M E N T A L.

(*p*-Tolyl)-methylglycide Ester (I).—Sodium ethoxide, prepared from sodium (6.5 g.) and alcohol (65 c.c.), was treated with petroleum ether (65 c.c.; b.p. 90°-100°) and the mixture slowly cooled with continuous shaking, when the ethoxide was obtained in fine suspension. To this suspension, thoroughly cooled in a freezing mixture, was added with shaking, a cooled solution of *p*-methylacetophenone (34.5 g. Nellor, *J. Amer. Chem. Soc.*, 1924, **46**, 1890) and chloroacetic ester (32 g.). The mixture was allowed to rise to room temperature slowly and after standing at ordinary temperature for 16 hours, was refluxed on the water-bath for 5 hours. The dark brown solution was decomposed with ice. The upper layer was taken up in ether and repeatedly washed with ice-cold dilute potassium hydroxide solution and then with water. After the removal of solvents and unchanged materials, the fraction boiling between 130° and 145°/5 mm. was collected. On redistillation, the glycide ester boiled at 130°-35°/5 mm., yield 37.5 g. (Found: C, 70.75; H, 7.1. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.2 per cent).

(*p*-Tolyl)-Propionaldehyde (II).—To an alcoholic solution of sodium ethoxide, prepared from sodium (3.7 g.) and alcohol (60 c.c.), the glycide ester (34.5 g.) was added with shaking. The mixture was cooled and to this water (3 c.c.) was added slowly with constant shaking; the mixture became hot and on continuous shaking, the whole mass became viscous and finally the crystalline sodium salt separated and the whole of the mixture solidified.

It was allowed to stand overnight. Absolute alcohol was added and the sodium salt was filtered off, washed with alcohol and ether, and next added to crushed ice and hydrochloric acid in a flask. A crystalline precipitate consisting of the free acid was perceptible for a moment. But decomposition set in immediately, an oil separating with copious evolution of carbon dioxide. The mixture was then subjected to steam distillation, the distillate extracted with ether, the ethereal extract dried (calcium chloride) and distilled. It had b. p. $92^{\circ}/6$ mm. (lit. $89^{\circ}\text{--}90^{\circ}/5$ mm.). The semicarbazone, after recrystallisation from alcohol, melted at 158° (lit. 156°). (Found: N, 20.8, 20.7. Calc. for $C_{11}H_{18}ON_3$: N, 20.5 per cent).

Ethyl γ -(p-Tolyl)- β -hydroxyvalerate (III).—A mixture of the aldehyde (17 g.), bromoacetic ester (30 g.) and zinc-wool (16 g., 2 mols.) was covered with dry benzene (75 c.c.). A crystal of iodine was added as a catalyst. On warming the mixture the reaction started and the vigour of the reaction was maintained until most of the zinc went into solution. Next it was heated for 1 hour on the water-bath. The solution was then decomposed with ice and sulphuric acid. Excess of zinc was filtered off and the benzene was thoroughly washed with ice-cold potassium hydroxide solution followed by water. From the dried (calcium chloride) solution, the hydroxy-ester was isolated by distillation, b. p. $149^{\circ}/5$ mm. as a slightly bluish fluorescent oil, yield 20 g. (Found: C, 71.35; H, 8.0. $C_{14}H_{20}O_3$ requires C, 71.18; H, 8.4 per cent).

Ethyl γ -(p-Tolyl)- Δ^{β} -pentenoate.—To a well cooled solution of the hydroxy-ester (III, 21 g.) in dry pyridine (15 c.c.) and dry ether (50 c.c.), thionyl chloride (7 c.c.) was added with shaking drop by drop. The mixture was allowed to stay at room temperature for 2 hours after the addition was complete in the cold and decomposed with ice and extracted with ether. The ethereal solution was thoroughly washed with acid and alkali. The crude residue left after evaporation of ether was diluted with benzene and heated on the water-bath with precipitated copper to remove sulphur. After removal of benzene, the residue was distilled in *vacuo* when a small fraction boiled below $145^{\circ}/5$ mm. There was a continuous rise in the boiling point and finally the whole of the substance polymerised in the flask. The fraction (5 g.), isolated above, was again subjected to a further distillation and a sample was collected boiling at $134^{\circ}\text{--}136^{\circ}/6$ mm. as a mobile oil having a yellowish tinge. (Found: C, 76.9; H, 7.8. $C_{14}H_{18}O_2$ requires C, 77.05; H, 8.2 per cent).

γ -(p-Tolyl)- Δ^{β} -pentenoic Acid (V).—A mixture of the aldehyde (38 g.) and malonic acid (15 g.) in pyridine (120 c.c.), and piperidine (4 c.c.) was heated on the water-bath for 3 hours and then on a sand-bath for 5 hours.

After decomposition with ice and sulphuric acid an oil separated which solidified to a crystalline mass. This was collected and freed from adhering oil on a porous tile, m. p. $78-81^{\circ}$, yield 30 g. After recrystallisation from petroleum ether it had m. p. $85^{\circ}-86^{\circ}$. (lit. m. p. 86°). (Found: C, 75.7; H, 7.1. $C_{12}H_{14}O_2$ requires C, 75.7; H, 7.3 per cent).

1 - Keto - 4 : 7-dimethyl-1 : 2 : 3 : 4 - tetrahydronaphthalene (VII),— γ -(*p*-Tolyl)-valeric acid (15.5 g.), obtained by reduction of the above acid through the lactone with phosphorus and hydriodic acid, was heated on the water-bath for $\frac{1}{2}$ hour with 85% H_2SO_4 (80 c.c.). The product was diluted with water after cooling and extracted with ether and the extract washed with sodium carbonate. The dried ($CaCl_2$) solution furnished the ketone, b. p. $118^{\circ}/4$ mm., yield 11 g. (Found: C, 83.01; H, 8.0. $C_{12}H_{14}O$ requires C, 82.7; H, 8.0 per cent).

The semicarbazone, prepared in the usual way, crystallised from petroleum ether, m. p. $195-96^{\circ}$. (Found: N, 18.2. $C_{13}H_{17}ON_3$ requires N, 18.18 per cent).

Cadalene (VIII).—To magnesium isopropyl iodide prepared with magnesium (2.5 g.) and isopropyl iodide (20 g.) in ether, was added with cooling the above ketone (9 g.) in ether and the mixture allowed to stand overnight, after which the reaction was completed by heating for 3 hours and finally the mixture decomposed with ice and hydrochloric acid. Isolated in the usual way a mobile liquid was obtained, b. p. $119^{\circ}/5$ mm., yield 7 g. It was a mixture of the hydroxy compound and its dehydration product. (Found: C, 87.3; H, 9.7. $C_{16}H_{22}O$ requires C, 82.5; H, 10.1; $C_{16}H_{20}$ requires C, 90.0; H, 10.0 per cent).

The above mixture (6 g.) was heated with selenium (2 g.) for 24 hours at 300° . After cooling, the whole mass was repeatedly extracted with ether. The residue from ether was distilled in *vacuo* and the distillate redistilled over sodium when a clear mobile liquid, b. p. $106^{\circ}/3$ mm., was obtained having a characteristic aromatic smell. (Found: C, 91.5; H, 8.8. Calc. for $C_{16}H_{18}$: C, 90.9; H, 9.09 per cent).

The picrate, prepared in the usual way, crystallised in golden yellow shining needles from alcohol, m. p. $114^{\circ}-15^{\circ}$ (lit. 115°). (Found: N, 9.8. Calc. for $C_{21}H_{21}O_7N_3$: N, 9.76 per cent).

My grateful thanks are due to Prof. P. C. Mitter for his kind interest in the work and for his valuable suggestions.



APPARENT MOLAL VOLUMES OF ELECTROLYTE MIXTURES IN AQUEOUS SOLUTION.

BY AMRITANSU SEKHAR CHAKRAVARTI AND BALBHADRA PRASAD.



The variation of apparent molal volume (ϕ) of an electrolyte with concentration is governed by the relation : $\phi = \phi_0 + k \sqrt{C}$ (at least for concentrations greater than 0.03 M) where ϕ_0 and k are constants. The apparent molal volume of a mixture of electrolytes at any concentration can be calculated as in the case of a single electrolyte, if the average molecular weight of the mixture is calculated from the mixture rule. It is found (a) that a mixture of electrolytes also obeys the above equation with the same limitations as a single electrolyte, and (b) that both ϕ_0 and k in case of mixtures are linear functions of the composition (molar percentage of any one of the components).

The apparent molal volumes of strong electrolytes were shown empirically to vary linearly with the square root of concentration by Masson (*Phil. Mag.*, 1929 *vii*, 8, 218) and Geffcken (*Naturwiss.*, 1931, 18, 321 ; *Z. physikal. Chem.*, 1931, 155, 1). Redlich and Rösenfeld deduced the same result from the interionic attraction theory (*Z. physikal. Chem.*, 1931, 155, 65). Their equation may be written as

$$\phi = \phi_0 + k \sqrt{C},$$

where ϕ denotes the apparent molal volume, ϕ_0 and k are constants characteristic of the solute and temperature. Redlich and Rösenfeld's theory predicts that the value of k should be the same for all strong electrolytes of the same valence type at extreme dilution. This, however, has not been borne out by the results of Srinivasan and Prasad (*Trans. Faraday Soc.*, 1939, 35, 1462) as well as by the data of Jones and Ray (*J. Amer. Chem. Soc.*, 1937, 59, 187) incorporated by the former authors in their paper. They find that the values of k of electrolytes of the same valence type are not the same, though generally of the same order. The square root law is also not strictly valid at extreme dilutions. Similar observations were made by the present authors with electrolytes of the 2-1 valent type (*Trans. Faraday Soc.*, 1939, 35, 1466). So far the case of mixtures of strong electrolytes has not engaged the attention of workers. The apparent molal volume of any mixture of two strong electrolytes may be calculated from the usual formula,

$$\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{\rho_0 C},$$

where M is the average molecular weight of the solute, C , the total concentration of solute, ρ and ρ_0 , the density of solution and water respectively. The average molecular weight, M of a mixed solute composed of electrolyte 1 of

molecular weight M_1 and electrolyte 2 of molecular weight M_2 in the molar ratio n_1 to n_2 can be readily obtained from the formula,

$$M = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

In case $n_1 : n_2$ is kept constant and the total concentration is varied, the average molecular weight is fixed.

It would be of interest to examine if the apparent molal volume (of solutions in which $n_1 : n_2$ is kept constant) thus obtained would follow the law : $\phi = \phi_0 + k\sqrt{C}$ and if it did, how the constants ϕ_0 and k would vary with composition and how they would be related to the values for the pure components. To clarify these points, apparent molal volumes of two mixtures with a common ion (K_2SO_4 and KCl ; $NaNO_3$ and $NaCl$) and two without a common ion ($NaNO_3$ and KCl ; $NaNO_3$ and HCl) were determined. Three different compositions were studied in each case. The constants ϕ_0 and k for pure K_2SO_4 and HCl were also determined. The values for pure KCl , $NaNO_3$ and $NaCl$ were taken from Srinivasan and Prasad's paper (*loc.cit.*).

EXPERIMENTAL.

The thermostat which was maintained at $35^\circ \pm 0.005$ has already been described (*J. Indian Chem. Soc.*, 1933, 12, 499; 1938, 16, 301). The procedure for density determination is the same as that described in the latter paper, except that the pyknometers used had volumes of about 64 and 55 c.c. and all the weights were reduced to vacuum standard by means of the formula,

$$W_v = W + (V_l + V_p - V_w)\rho$$

where ρ is the density of air, W_v , the weight in vacuum, W , the weight in air, V_w , V_l and V_p , the volumes of weights, liquid and pyknometer, the last being given by the quotient of weight of pyknometer/density of glass. The density of air was measured every day by using the formula,

$$\rho = (W_1 - W_2)/V,$$

where W_1 and W_2 are the weights of a sealed flask in vacuum and air respectively and V is its external volume (535.5 c.c.). V was found by weighing the flask in air and water without applying any buoyancy correction. In order to know W_1 , one direct determination of the density of air was made. The density figures are the results of two determinations, agreeing with each other within 1 mg. The experimental error is not expected to exceed sixteen parts in a million.

In the following table, C indicates the total concentration in gram moles per litre, ρ , the density in g. per c.c. and ϕ , the apparent molal volume in c.c. The figures for pure K_2SO_4 and HCl are given first.

TABLE I.

C .	ρ .	ϕ .	C .	ρ .	ϕ .
K_2SO_4 . $\phi = 51.5 + 7.28 \sqrt{C}$.			HCl . $\phi = 18.2 + 1.00 \sqrt{C}$.		
0	0.994058	—	0	0.994058	—
0.0100	0.995262	54.00	0.0020	0.994087	22.09
0.0200	0.996490	54.79	0.0040	0.994127	19.33
0.0300	0.997705	54.82	0.0070	0.994170	20.58
0.0400	0.998921	54.81	0.0100	0.994233	19.04
0.0500	1.000141	54.72	0.0150	0.994315	19.44
0.0600	1.001345	53.27	0.0500	0.994949	18.75
0.0700	1.002540	53.22	0.1000	0.995834	18.81
0.2000	1.017950	54.93	0.2000	0.997657	18.58
0.5000	1.052001	56.73	0.5000	1.002854	18.98
$[K_2SO_4] / [KCl] = 3 : 1$.			$[K_2SO_4] / [KCl] = 1 : 1$.		
$\phi = 45.5 + 5.71 \sqrt{C}$.			$\phi = 39.6 + 4.29 \sqrt{C}$.		
0.0100	0.995102	45.24	0.0100	0.994921	38.22
0.0200	0.996115	46.60	0.0200	0.995779	40.46
0.0300	0.997165	45.89	0.0300	0.996595	39.96
0.0400	0.998176	46.51	0.0400	0.997402	40.91
0.0500	0.999205	46.53	0.0500	0.998243	40.83
0.0600	1.000232	46.56	0.0600	0.999086	40.73
0.0700	1.001254	46.65	0.0700	0.999920	40.79
0.2000	1.014351	48.01	0.2000	1.010647	41.60
0.5000	1.043934	49.72	0.5000	1.035065	42.53
$[K_2SO_4] / [KCl] = 1 : 3$.			$[NaNO_3] / [NaCl] = 3 : 1$.		
$\phi = 34.0 + 2.86 \sqrt{C}$.			$\phi = 27.4 + 1.00 \sqrt{C}$.		
0.0100	0.994688	36.58	0.0100	0.994565	27.84
0.0200	0.995341	35.43	0.0200	0.995055	28.69
0.0300	0.995997	34.94	0.0300	0.995560	28.48
0.0400	0.996640	35.02	0.0400	0.996064	28.38
0.0500	0.997282	35.09	0.0500	0.996569	28.32
0.0600	0.997950	34.70	0.0600	0.997095	27.92
0.0700	0.998596	34.75	0.0700	0.997628	27.54
0.2000	1.006900	35.37	0.0900	0.998601	28.06
0.5000	1.025813	36.02	0.1200	1.000144	27.82
			0.1600	1.002134	28.06
			0.2000	1.004156	28.06
			0.4000	1.014155	28.30
			0.6000	1.024202	28.30

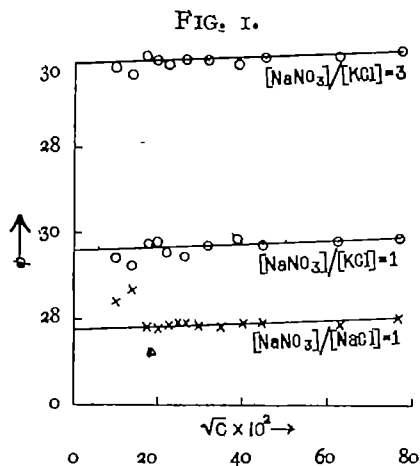
TABLE I (contd.).

C.	ρ .	ϕ .	C.	ρ .	ϕ .
[NaNO ₃] / [NaCl] = 1 : 1.			[NaNO ₃] / [NaCl] = 1 : 3.		
$\phi = 24.4 + 1.00 \sqrt{C}$.			$\phi = 21.4 + 1.00 \sqrt{C}$.		
0.0100	0.994516	26.09	0.0100	0.994466	24.45
0.0200	0.994982	26.77	0.0200	0.994921	22.08
0.0300	0.995476	24.61	0.0300	0.995340	22.50
0.0400	0.995955	24.45	0.0400	0.995768	22.48
0.0500	0.996414	24.76	0.0500	0.996211	22.17
0.0600	0.996878	24.88	0.0600	0.996652	22.00
0.0700	0.997358	24.74	0.0700	0.997120	21.49
0.0900	0.998301	24.73	0.0900	0.997978	21.67
0.1200	0.999281	24.65	0.1200	0.999725	21.71
0.1600	1.001597	24.77	0.1600	1.001013	21.76
0.2000	1.003467	24.83	0.2000	1.002745	21.80
0.4000	1.012911	24.75	0.4000	1.011198	22.38
0.6000	1.022074	25.19	0.6000	1.019863	22.22
[NaNO ₃] / [KCl] = 3 : 1.			[NaNO ₃] / [KCl] = 1 : 1.		
$\phi = 29.7 + 1.25 \sqrt{C}$.			$\phi = 29.0 + 1.25 \sqrt{C}$.		
0.0100	0.994587	29.64	0.0100	0.994572	28.53
0.0200	0.995124	29.25	0.0200	0.995095	28.06
0.0300	0.995624	30.35	0.0300	0.995575	29.35
0.0400	0.996156	30.09	0.0400	0.996075	29.50
0.0500	0.996697	29.77	0.0500	0.996614	28.80
0.0700	0.997723	30.19	0.0700	0.997646	28.66
0.1000	0.999302	30.11	0.1000	0.999126	29.24
0.1500	1.001962	29.85	0.1500	1.001588	29.72
0.2000	1.004515	30.26	0.2000	1.004193	29.25
0.4000	1.014940	30.34	0.4000	1.014180	29.61
0.6000	1.025157	30.72	0.6000	1.024220	29.77
[NaNO ₃] / [KCl] = 1 : 3			[NaNO ₃] / [HCl] = 3 : 1.		
$\phi = 28.8 + 1.38 \sqrt{C}$.			$\phi = 28.1 + 1.00 \sqrt{C}$.		
0.0100	0.994534	29.68	0.0100	0.994470	32.15
0.0200	0.995043	28.01	0.0200	0.994926	29.64
0.0300	0.995505	29.04	0.0300	0.995397	28.40
0.0400	0.995969	29.50	0.0400	0.995865	27.86
0.0500	0.996487	28.69	0.0500	0.996301	28.17
0.0700	0.997452	29.78	0.0700	0.997193	28.25
0.1000	0.998832	29.53	0.1000	0.998532	28.29
0.1500	1.001263	29.24	0.1500	1.000738	28.50
0.2000	1.003588	29.62	0.2000	1.002948	28.58
0.4000	1.013078	29.73	0.4000	1.011717	28.89
0.6000	1.022581	29.74	0.6000	1.020517	28.99

TABLE I (contd.).

C.	ρ .	ϕ .	C.	ρ .	ϕ .
[NaNO ₃] / [HCl] = 1 : 1.			[NaNO ₃] / [HCl] = 1 : 3.		
$\phi = 24.6 + 1.00 \sqrt{C}$			$\phi = 21.5 + 1.00 \sqrt{C}$		
0.0100	0.994394	27.30	0.0100	0.994293	25.25
0.0200	0.994727	27.45	0.0200	0.994563	25.49
0.0300	0.995090	26.49	0.0300	0.994858	22.06
0.0400	0.995471	25.56	0.0400	0.995131	21.91
0.0500	0.995852	25.01	0.0500	0.995417	21.55
0.0700	0.996598	24.60	0.0700	0.995955	21.63
0.1000	0.997639	25.08	0.1000	0.996738	21.93
0.1500	0.999444	24.98	0.1500	0.998083	21.90
0.2000	1.001240	24.98	0.2000	0.999431	21.86
0.4000	1.008393	25.05	0.4000	1.004760	21.97
0.6000	1.015375	25.36	0.6000	1.009997	22.16

Some of the results are shown graphically in the following figure. The apparent molal volume is plotted against the square root of concentration.



The figure shows that the results are represented by straight lines. There are, however, some discrepancies at the lowest concentrations in many cases. This is in keeping with the similar observations made in this laboratory in the cases of single electrolytes (*loc. cit.*). It may be said that for concentrations greater than 0.03M, the variation of ϕ with \sqrt{C} is linear, and the great sensitiveness of ϕ at low concentrations to small error in density measurements may be responsible for the discrepancies. But it is hardly likely that all these

divergences, many of which are beyond experimental errors and which are almost always on the same side, are due to density errors. At any rate, above concentrations of 0.03M, the equation: $\phi = \phi_0 + k\sqrt{C}$ holds good. The discrepancies are not very glaring because very low concentrations have been avoided.

The values of the constants ϕ_0 and k are tabulated below, those for pure KCl, NaCl and NaNO₃ being taken from Srinivasan and Prasad's paper (*loc. cit.*).

TABLE II.

Solute composition.	ϕ_0 .	k .	Solute composition.	ϕ_0 .	k .
Pure K_2SO_4	51.5	7.28	Pure $NaNO_3$	30.3	1.27
$[K_2SO_4] / [KCl] = 3$.	45.5	5.71	$[NaNO_3] / [NaCl] = 3$.	27.4	1.00
$[K_2SO_4] / [KCl] = 1$.	39.6	4.29	$[NaNO_3] / [NaCl] = 1$	24.4	1.00
$[K_2SO_4] / [KCl] = 1/3$	34.0	2.86	$[NaNO_3] / [NaCl] = 1/3$	21.4	1.00
Pure KCl	28.4	1.50	Pure $NaCl$	18.1	1.24
Pure $NaNO_3$	30.3	1.27	Pure $NaNO_3$	30.3	1.27
$[NaNO_3] / [KCl] = 3$.	29.7	1.25	$[NaNO_3] / [HCl] = 3$.	28.1	1.00
$[NaNO_3] / [KCl] = 1$.	29.0	1.25	$[NaNO_3] / [HCl] = 1$.	24.6	1.00
$[NaNO_3] / [KCl] = 1/3$.	28.8	1.38	$[NaNO_3] / [HCl] = 1/3$.	21.5	1.00
Pure KCl	28.4	1.50	Pure HCl	18.2	1.00

Figure 2 shows the variation of ϕ_0 and Figure 3 of k with composition.

FIG. 2.

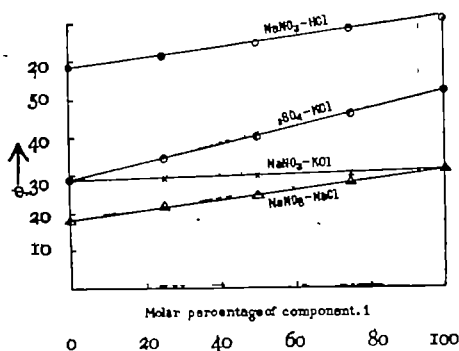
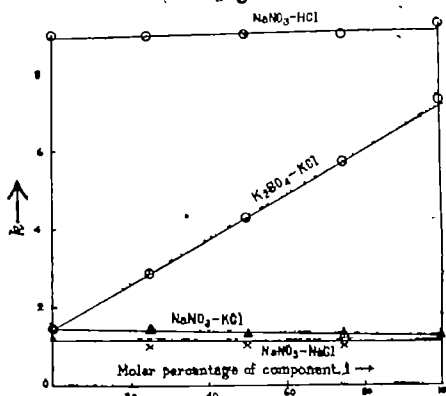


FIG. 3.



It is evident that the variation of both ϕ_0 and k with the composition of the mixture is approximately linear. The slight divergence may be considered well within the limits of experimental error. Thus, we can express these quantities by the simple equations: $\phi_0 = x\phi_0' + (1-x)\phi_0''$; $k = xk' + (1-x)k''$. Here, ϕ_0 and k refer to the mixture, ϕ_0' and k' to the pure first component and ϕ_0'' and k'' to the second component. " x " indicates the fractional molar concentration of the first component [$x = C_1 / (C_1 + C_2)$] where C_1 and C_2 are the concentrations of the pure first and second component respectively at a total concentration C .

Our thanks are due to the Government of Orissa for the award of a Research Scholarship to one of us (A.S.C.) during the tenure of which this piece of work was carried out.

MAYURBHANJ CHEMICAL LABORATORY,
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Received January 23, 1941.

IODINATION. PART II. STUDIES ON THE IODINATION OF DIFFERENT UNSATURATED ORGANIC COMPOUNDS IN THE DARK IN DIFFERENT NON-POLAR SOLVENTS.

By J. C. GHOSH, S. K. BHATTACHARYYA, M. M. DUTT
AND M. J. RAO.

Investigations on the velocity of addition of iodine to β -amylene and d -pinene in the dark in presence of non-polar solvents have shown that the reaction is termolecular with respect to iodine but unimolecular with respect to the acceptor, *i.e.*, it is quadrimolecular with respect to both. The rate of reaction is not much affected by increase of temperature or by increase in the reaction surface, but it appears to depend to a great extent upon the nature of the solvent.

In this part the results of investigations on the velocity of addition of iodine to β -amylene and d -pinene in the dark in non-polar solvents, *e.g.*, carbon tetrachloride, benzene and carbon disulphide have been described.

EXPERIMENTAL.

The reagents are purified exactly in the same way as has been described in Part I of this series (this Journal, 1941, **18**, 171). Fresh solutions were prepared after every 2 days with freshly distilled β -amylene and d -pinene to avoid any formation of peroxide which vitiates the kinetic measurements.

Determination of the Velocity of Reaction.

The reaction cell ($4 \times 4 \times 1$ c.c.) made of plane glass plates fused into one another with a stopper at the top was placed inside a double jacketed metal box wholly covered by means of black cloth so that no light could pass inside the box. The temperature was kept constant by passing, with the help of a circulating pump, water from a thermostat through the annular space of the box,

The velocity of reaction was determined by pipetting out 0.66 c.c. of the reaction mixture by means of a micropipette and titrating iodometrically with 0.01N-thiosulphate solution by means of a microburette.

The reaction was studied at different temperatures. For low temperatures an ice-bath was used.

To see the effect of surface on the velocity of reaction, experiments were carried out in presence of quartz sands and glass beads. For this, these were carefully cleaned by washing successively with chromic acid, dilute NaOH, dilute HCl, water and finally by steaming. The experiments were carried out in the reaction cell packed with different amounts of quartz sands or beads.

To see the effect of hydriodic acid on the rate of reaction, saturated solutions of HI in benzene, carbon tetrachloride and carbon disulphide were prepared and used in the experiments. It is to be pointed out that HI has practically very little effect on the reaction rate.

The experimental results on the iodination of β -amylene and *d*-pinene are recorded in Tables I to VIII.

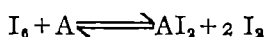
The velocity of reaction was found to be proportional to the concentration of the acceptor and to the cube of the iodine concentration, i.e., the active molecule is probably I_3 . Gróh and Szelestey (*Z. anorg. Chem.*, 1927, **162**, 333) and Gróh and Takacs (*Z. physikal. Chem.*, 1930, **149**, 195) have shown that in non-polar solvents I_3 molecules are in equilibrium with I_2 molecules according as



so that

$$[I_3] = C[I_2]^3.$$

The reaction between iodine and the acceptor may be represented in the following way :—



so that

$$\begin{aligned} \frac{dx}{dt} &= k''[I_3][A] - k'[AI_3][I_2]^2 \\ &= k[I_2]^3[A] - k'[AI_3][I_2]^2. \end{aligned}$$

Algebraically the velocity of reaction can be represented as

$$\frac{dx}{dt} = k(a-x)^3(b-x) - k'x(a-x)^2 \quad \dots (i)$$

where a and b are the initial concentrations of iodine and the acceptor respectively in gram mols per litre and x is the concentration of the iodo-product in gram mols per litre at any time t (min).

At equilibrium,

$$k(a-x_1)^2(b-x_1) = k'(a-x_1)^2x_1$$

where x_1 is the concentration of the iodo product when equilibrium is established.

$$\text{Therefore, } K_F = \frac{k}{k'} = \frac{(a-x_1)^2 \cdot x_1}{(a-x_1)^2(b-x_1)} = \frac{x_1}{(a-x_1)(b-x_1)} \quad \dots (ii)$$

where K_F is the equilibrium constant.

From (i) we have

$$\frac{dx}{(a-x)^2[k(a-x)(b-x) - k'x]} = dt$$

or

$$\frac{dx}{(a-x)^2(\xi_1-x)(\xi_2-x)} = kdt \quad \dots (iii)$$

where ξ_1 and ξ_2 are the roots of the equation

$$x^2 - \frac{kb+ka+k'}{k}x + ab = 0. \quad \dots (iv)$$

From (iv) on solving we get $\xi_1 = \frac{ab}{x_1}$ and $\xi_2 = x_1$, where x_1 is the concentration of the reaction product at equilibrium. Now, in order to integrate (iii) we must resolve the fraction

$$\frac{1}{(a-x)^2(\xi_1-x)(\xi_2-x)}$$

into partial fractions thus

$$\frac{1}{(a-x)^2(\xi_2-x)(\xi_1-x)} = \frac{A}{(a-x)^2} + \frac{A_1}{(a-x)} + \frac{B}{(\xi_1-x)} + \frac{C}{(\xi_2-x)}$$

where A , A_1 , B , and C are constants.

From this identity on reduction to a common denominator, we get on equating coefficients of like powers in the two numerators the values of these constants as

$$A = \frac{1}{(\xi_1 - a)(\xi_2 - a)};$$

$$A_1 = \frac{2a - (\xi_1 + \xi_2)}{(\xi_1 - a)^2(\xi_2 - a)^2};$$

$$B = \frac{1}{(a - \xi_1)^2(\xi_2 - \xi_1)};$$

and

$$C = \frac{1}{(a - \xi_2)^2(\xi_1 - \xi_2)}.$$

Hence
$$\int \frac{dx}{(a-x)^2(\xi_1-x)(\xi_2-x)} = \int k dt$$

or
$$A \int \frac{dx}{(a-x)^2} + A_1 \int \frac{dx}{(a-x)} + B \int \frac{dx}{(\xi_1-x)} + C \int \frac{dx}{(\xi_2-x)} = \int k dt$$

or
$$\frac{A}{(a-x)} - A_1 \ln(a-x) - B \ln(\xi_1-x) - C \ln(\xi_2-x) = kt + \text{constant}.$$

In the initial stages when $t=0$ and $x=0$

$$\frac{A}{a} - A_1 \ln a - B \ln \xi_1 - C \ln \xi_2 = \text{constant}.$$

Therefore

$$\frac{A.x}{2.303(a-x).a} + A_1 \log \frac{a}{a-x} + B \log \frac{\xi_1}{\xi_1-x} + C \log \frac{\xi_2}{\xi_2-x} = \frac{kt}{2.303}$$

i.e., $k =$

$$\frac{2.303}{t} \left[\frac{A.x}{2.303(a-x).a} + A_1 \log \frac{a}{a-x} + B \log \frac{\xi_1}{\xi_1-x} + C \log \frac{\xi_2}{\xi_2-x} \right] \dots \quad (v)$$

The velocity constants have been calculated from the relation (v) which has been found to hold good very satisfactorily.

R E S U L T S.

A few typical experiments are recorded below.

TABLE I.

Acceptor = β -amylene. Solvent = CCl_4 . Temp. (θ) = 30° .

EXPT. 1.			EXPT. 2.		
$a = 0.0665M$; $b = 0.1M$; $K_E = 5.7$; $x_1 = 0.0208M$.			$a = 0.08135M$; $b = 0.1M$; $K_E = 5.7$; $x_1 = 0.02453M$.		
t	$a-x$	k	t	$a-x$	k
0	0.0665		0	0.08135	
10	0.0635	11.6	7	0.0775	11.7
25	0.0603	11.2	12	0.0753	11.8
45	0.0571	11.4	25	0.0717	11.5
mean 11.4			mean 11.7		

EXPT. 3.			EXPT. 4.		
$a = 0.04005M$; $b = 0.2M$; $K_E = 5.7$; $x_1 = 0.02105M$.			$a = 0.083M$; $b = 0.2M$; $K_E = 5.7$; $x_1 = 0.03966M$.		
t	$a-x$	k	t	$a-x$	k
0	0.04005		0	0.083	
15	0.03812	11.1	10	0.073	11.7
40	0.03578	10.5	25	0.06586	10.4
70	0.03375	10.1	45	0.0595	10.5
mean 10.6			mean 10.9		

Similar calculations were made in all the experiments and the results are summarised in Tables II to VIII.

Effect of varying the Concentrations of Reactants.

TABLE II.

Temp. = 30° . Acceptor = β -amylene.

Solvent: CCl_4			Solvent: C_6H_6			Solvent: CS_2		
a	b	k	a	b	k	a	b	k
0.083M	0.2M	10.9	0.1M	0.198M	15.1	0.0776M	0.178M	3.8
0.0536	"	11.9	0.075	"	15.1	0.066	"	3.7
0.04005	"	10.6	0.05	"	15.0	0.0523	"	3.8
0.0268	"	10.3	0.025	"	15.4	0.039	"	4.1
0.08135	0.1	11.7	0.075	0.099	15.3	0.0523	0.355	4.0
0.0665	"	11.4	0.05	"	15.1	"	0.267	3.8
0.0334	"	11.6	0.025	"	15.2	"	0.089	3.8
0.0542	0.3	11.2	0.05	0.297	15.6			
"	0.2	11.3	"	0.149	16.0			
"	0.1	11.8						
"	0.05	11.7						

TABLE III.

Solvent = CCl_4 . Temp. = 29° . Acceptor = Pinene.

a.	b.	$k \times 10^{-1}$.	a.	b.	$k \times 10^{-1}$
0'01475M	0'04M	18.6	0'0418	0'08	18'6
0'0211	„	18.2	0'0627	„	19'5
0'0295	„	19'3	0'0211	0'02	19'3
0'0209	0'08	17'4	„	0'03	18'6
			„	0'06	18'7

TABLE IV.

Temp. = 21° . Acceptor = Pinene.

Solvent: C_6H_6 .			Solvent: CS_2 .		
a.	b.	$k \times 10^{-1}$.	a.	b.	$k \times 10^{-1}$
0'02078M	0'08M	89'9	0'02M	0'08M	10.2
0'03905	„	92'1	0'04	„	10'3
0'062	„	90'4	0'06	„	10'5
0'02078	0'02	92'4	0'02	0'02	10'0
„	0'04	92'5	„	0'03	10'1
„	0'06	90'9	„	0'04	10'5
			„	0'06	10.8

Effect of Temperature.

TABLE V.

Acceptor = β -amylene.

Solvent: CCl_4 .			Solvent: C_6H_6 .			Solvent: CS_2 .		
θ .	b.	k.	θ .	b.	k.	θ .	a.	k.
$a = 0'0542M$.			$a = 0'075M$.			$b = 0'1785M$.		
30'0	0'2M	11.3	30'0	0'198M	15.1	30'0	0'078M	3.8
8'0	„	9'9	9'0	„	15'1	6'0	„	3'6
30'0	0'1	11'8	30'0	0'099	15'3	30'0	0'066	3'7
8'0	„	10'5	9'0	„	15'4	6'0	„	3'7

TABLE VI.

Acceptor = Pinene

Solvent: CCl ₄ .			Solvent: C ₆ H ₆ .			Solvent: CS ₂ .		
θ .	a .	$k \times 10^{-1}$.	θ	b	$k \times 10^{-1}$.	θ .	a .	$k \times 10^{-1}$.
	$b = 0.08M$.			$a = 0.02078M$.			$b = 0.08M$.	
29° 0	0.0209M	17.4	21° 0	0.08M	89.9	21° 0	0.02M	10.2
0° 0	"	17.4	8° 0	"	93.3	8° 0	"	10.6
29° 0	0.0418	18.6	21° 0	0.04	92.5	21° 0	0.04	10.3
0° 0	"	19.8	8° 0	"	92.5	8° 0	"	11.2

Effect of Increasing the Surface.

TABLE VII.

Acceptor = β -amylene.

Solvent.	θ .	Quartz sand.	a .	b .	k
CCl ₄	30°	Nil.	0.0542M	0.3M	11.2
	"	6 g.	"	"	13.3
	"	9	"	"	13.4
C ₆ H ₆	"	Nil	0.05	0.297	15.6
	"	9	"	"	11.8
CS ₂	"	Nil	"	0.2	3.8
	"	9	"	"	4.1

TABLE VIII.

Acceptor = Pinene.

Solvent.	θ .	Nature of surface.	a .	b .	$k \times 10^{-1}$.
C ₆ H ₆	21°	Without bead or sand	0.02078M	0.08M	89.9
"	"	With glass bead (9 g.)	"	"	80.2
"	"	With quartz sand (9 g.)	"	"	77.3

The Tables VII and VIII show that the reaction velocity is not much affected by the increase in surface. It is to be mentioned here that the quartz sands taken were so large in amount that there was no free liquid of the reaction mixture over the surface of sand and the entire liquid was in a thin film over the surface of the sand particles.

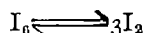
DISCUSSION.

The reaction has the following characteristics :—

1. The reaction is termolecular with respect to iodine and unimolecular with respect to the acceptor, i.e., it is quadrimolecular with respect to both.
2. The reaction rate is much less affected by increase or decrease in temperature. According to the Von Halban-Dhar rule polymolecular reactions have, as a rule, smaller temperature coefficients than unimolecular ones. This rule seems applicable to the cases investigated in this paper.
3. The reaction rate is much less affected by increase in reaction surface which indicates that the reaction is homogeneous.
4. The rate of the reaction depends to a great extent on the nature of solvent. It is greatest in C_6H_6 and least in CS_2 .

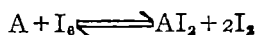
The following mechanism will explain the observed facts.

We can assume according to the observations made by Grøh *et al* (*loc. cit.*) that in non-polar solvents like CCl_4 , C_6H_6 and CS_2 iodine molecules (I_2) exist in equilibrium with hexa-atomic iodine molecules (I_6) in the following way :—



Now these I_6 molecules are responsible for the thermal iodination.

The reaction may be expressed by



so that

$$\begin{aligned} \frac{dx}{dt} &= k''[I_6][A] - k'[AI_2][I_2]^2 \\ &= k[I_2]^3[A] - k'[AI_2][I_2]^2 \\ &= k(a-x)^3(b-x) - k'.x.(a-x)^2 \end{aligned} \quad \dots (I)$$

where a and b are the initial concentrations of iodine and the acceptor respectively and x , the concentration of the iodo product in time t minute.

The equation (I) has been found to be very satisfactory.

As regards the influence of solvents used in this investigation, in benzene the velocity is considerably greater than for the other non-polar solvents. This difference is difficult to explain as all the three non-polar solvents have low dielectric constants.

IODINATION. PART III. STUDIES ON THE IODINATION OF DIFFERENT UNSATURATED ORGANIC COMPOUNDS IN THE DARK IN POLAR SOLVENTS.

BY S. K. BHATTACHARYYA AND M. J. RAO.

Velocity of addition of iodine to β -amylene and phenylacetylene in the dark in polar solvents, *e.g.*, ethyl alcohol and acetic acid, has been investigated. The reaction is termolecular with respect to both iodine and the acceptor. The reaction rate appears to be greater in alcoholic solution than in acetic acid. The temperature coefficient of the reaction rate is not high.

In this part the results of investigations on the velocity of addition of iodine to β -amylene and phenylacetylene in the dark in polar solvents like ethyl alcohol and acetic acid have been described.

EXPERIMENTAL.

The experimental arrangement and a major portion of the experimental procedure have been described in Parts I and II of this series.

Merck's extra pure absolute alcohol was further purified by distillation over metallic calcium before use. Merck's extra pure acetic acid was redistilled before use. B.D.H. phenylacetylene was used after further distillation. Fresh solutions were prepared after every 2 days with freshly distilled β -amylene and phenylacetylene.

The experimental results are recorded in Tables I to V. The velocity of the reaction was found to be proportional to the concentration of the acceptor and to the square of the iodine concentration. The velocity constant was calculated from the equation,

$$\frac{dx}{dt} = k_3(a-x)^2(b-x) \quad \dots (i)$$

where a and b are the initial concentrations of iodine and the acceptor respectively in gram mols per litre and x , the concentration of the iodo product in gram mols per litre in time t (mins.).

From equation (i) by integration we get

$$k_3 = \frac{1}{t(b-a)^2} \left\{ \frac{(b-a)x}{a(a-x)} + \log \frac{b(a-x)}{a(b-x)} \right\} \quad \dots (ii)$$

The relation (ii) was used when $(b-a)$ was considerable. For nearly equimolar mixtures, when $(b-a)$ was very small, the expression (iii) was used.

$$k_3 = \frac{1}{t} \left[\frac{1}{2} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} - \frac{b-a}{3} \left(\frac{1}{(a-x)^3} - \frac{1}{a^3} \right) + \dots \right] \quad \dots (iii)$$

The reactions between iodine and β -amylene and iodine and phenylacetylene do not proceed to completion and so the velocity constants were found to decrease with the progress of the reaction. In the earlier stages of the reaction, the amount of di-iodo product formed is negligible. In the following paper the velocity constants are recorded for 10% conversion in the case of β -amylene and 4% in the case of phenylacetylene. For this, graphs were drawn of concentrations of iodine against time and from the graphs times for the respective conversion were found out. This is to ensure the condition that the reverse reaction does not vitiate our results.

R E S U L T S.

Two typical experiments are recorded below.

TABLE I.

Expt. I. Acceptor= β -amylene. Solvent=EtOH.				Expt. II. Acceptor= β -amylene. Solvent=Acetic acid.			
$a=0.0482M.$		$b=0.107M.$		$a=0.046M.$		$b=0.1M.$	
Temperature= 31° .				Temperature= 31° .			
$t.$	$a-x$	t (for 10% conversion).	k_3	$t.$	$a-x$	t (for 10% conversion).	k_3
0	0.0482			0	0.0460		
5	0.0444	7.25 min.	4.4	20	0.0425	31.0 min.	1.2
15	0.0412			40	0.0407		
30	0.0390						

Similar calculations were made in all the experiments and the results are summarised in Tables II to V.

Effect of varying the Concentrations of the Reactants.

TABLE II.

Acceptor= β -amylene. Temperature= 31° .					
$a.$	$b.$	k_3	$a.$	$b.$	k_3
	Ethyl alcohol.			Ethyl alcohol.	
0.05M	0.214M	4.0	0.075	0.082	4.5
0.05	0.107	4.4	0.025	0.0268	4.7
0.0482	0.107	4.4		Acetic acid.	
0.0375	"	4.0	0.03	0.1	1.1
0.0125	"	4.3	"	0.075	1.0
0.075	0.0535	4.9	"	0.05	1.0
0.05	"	3.7	0.046	0.1	1.2
0.025	"	4.0	0.0466	0.05	1.1
			0.025	0.025	1.2

TABLE III.

Acceptor = Phenylacetylene. Temp = 21.5°. Solvent = Ethyl alcohol.

<i>a.</i>	<i>b.</i>	$k_3 \times 10^3.$	<i>a.</i>	<i>b.</i>	$k_3 \times 10^3.$
0.0625 <i>M</i>	0.111 <i>M</i>	11.3	0.0461	0.0167 <i>M</i>	11.2
0.0461	"	11.2	0.0234	"	11.5
0.0300	"	11.3	0.0300	0.055	10.5
0.0234	"	10.3	0.0234	"	11.0

Effect of Temperature.

TABLE IV.

Acceptor = β -amylenes.

Solvent.	$\theta.$	<i>a.</i>	<i>b.</i>	$k_3.$	<i>v.</i>
Ethyl alcohol	31.0	0.025 <i>M</i>	0.0535 <i>M</i>	4.0	
"	6.0	"	"	0.3	1.90
"	31.0	0.05	0.107	4.4	
"	6.0	"	"	0.8	1.98
Acetic acid	31.0	0.03	0.1	1.1	
"	11.0	"	"	0.6	1.35

v = temperature coefficient for 10° rise

$$= \left(\frac{k_{31}}{k_6} \right)^{\frac{10}{25}} \text{ in the case of ethyl alcohol as solvent}$$

$$= \left(\frac{k_{31}}{k_{11}} \right)^{\frac{10}{20}} \text{ in the case of acetic acid as solvent.}$$

TABLE V.

Acceptor = Phenylacetylene. Solvent = Ethyl alcohol.

θ	<i>a.</i>	<i>b.</i>	$k_3 \times 10^3 = k.$	<i>v.</i>
21.5	0.046 <i>M</i>	0.167 <i>M</i>	11.2	
11.5	"	"	6.1	1.84

$$v = \text{the temperature coefficient for } 10^\circ = \left(\frac{k_{21.5}}{k_{11.5}} \right)$$

DISCUSSION.

The reactions have the following characteristics :—

1. The reaction velocity is proportional to the concentration of the acceptor and to the square of the concentration of iodine, i.e., the reaction is termolecular with respect to both.

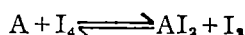
2. The temperature coefficient for a 10° rise is not high being less than 2.0. It is greater in alcoholic solutions than in acetic acid.

3. The rate of the reaction is greater in alcoholic solution than in acetic acid.

The following mechanism will explain the observed facts.

We may assume according to the observations made by Loeb (*J. Chem. Soc.*, 1888, 53, 805) that in polar solvents like alcohol and acetic acid, iodine molecules exist as I_4 .

The reaction may be represented by the equation,



so that

$$\begin{aligned} \frac{dx}{dt} &= k_3[A][I_4] - k'[AI_2][I_2] \\ &= k_3[A][I_2]^2 - k'[AI_2][I_2] \\ &= k_3(b-x)(a-x)^2 - k'x(a-x) \\ &= k_3(a-x)^2(b-x) - k'(a-x)x. \end{aligned}$$

In the initial stages of the reaction when x is very small

$$\frac{dx}{dt} = k_3(a-x)^2(b-x) \quad \dots (i)$$

where a and b are the initial concentrations of iodine and the acceptor respectively and x , the concentration of the iodo product at any time t .

The equation (i) has been found to hold good very satisfactorily. The increase in velocity of reaction for a 10° rise in temperature is of the order of 1.8 which is very much greater than the values observed in non-polar solvents. This in itself lends support to the view that the mechanisms of the reaction in the two types of solvents are different.

Our thanks are due to Dr. J. C. Ghosh, D.Sc. for his valuable suggestions and kind interest in the work.

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Received February 3, 1941

IODINATION. PART IV. STUDIES ON THE PHOTO- IODINATION OF DIFFERENT UNSATURATED ORGANIC COMPOUNDS IN LIGHT OF DIFFERENT FREQUENCIES IN NON-POLAR SOLVENTS.

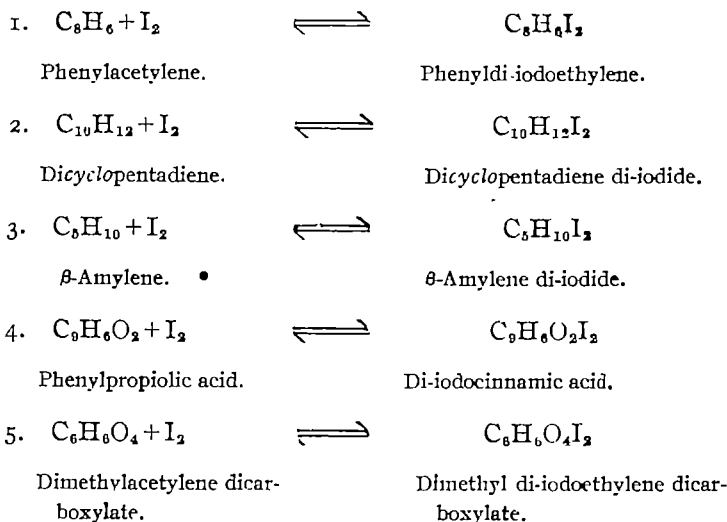
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Photochemical iodination of phenylacetylene, dicyclopentadiene, dimethylacetylene dicarboxylate, β -amylene and phenylpropionic acid in 546, 436 and 366 μ in solutions of Cl_4 has been described. The reaction is unimolecular with respect to iodine. The rate of reaction has a small temperature coefficient. The quantum efficiency of the reaction has been worked out to be high in the case of phenylacetylene and dicyclopentadiene but small in other cases.

Instances of photochemical iodination in non-polar solvents are rarely met with in literature. A short note on the photochemical formation of ethylene iodide in red light in solution of carbon tetrachloride published by De, Right and Wiig (*J. Amer. Chem. Soc.*, 1936, **58**, 693), the photochemical decomposition of ethylene iodide studied by Schumacher and co-workers (*Z. physikal. Chem.*, 1930, **B 11**, 45 ; 1931, **B 12**, 348), the photochemical iodination of butene, propylene and ethylene at very low temperature in 644, 546 and 436 μ in solutions of chloroform and carbon tetrachloride studied by Forbes and Nelson (*J. Amer. Chem. Soc.*, 1936, **58**, 182; 1937, **59**, 693) and the vapour phase photoreaction between cyclopropane and iodine at temperature a range of 180°-230°, studied by Ogg and Priest (*J. Chem. Phys.*, 1939, **7**, 736), are the only instances known. All these authors found that the reaction in light was simple and proceeded by a chain reaction started by iodine atoms formed by absorption of light.

In this part the results of investigations made on the photochemical iodination of phenylacetylene, dicyclopentadiene, dimethylacetylene dicarboxylate, β -amylene and phenylpropionic acid in 546, 436 and 366 μ in solutions of carbon tetrachloride have been described. It is to be pointed out here that the above reactions are reversible and do not proceed to completion except the photoreaction between iodine and phenylacetylene in

solution of carbon tetrachloride which goes almost to completion. The reactions may be represented according to the following equations :—



E X P E R I M E N T A L.

The light source was a quartz-mercury point-o-lite lamp run at 2.1 amperes from a battery of 30 volts. Parallel beams of light were obtained by using quartz convex lenses of different focal lengths. Monochromatic radiations of 546, 436 and 366 μ were obtained by using as filters, a dilute solution of copper sulphate (2%) in combination with the corresponding "Schott and Gen" monochromatic filters.

The reaction cell (4 \times 4 \times 0.5 c.c. or 4 \times 4 \times 0.3 c.c.) made of glass plates fused into one another with a stopper at the top was placed inside a double jacketed metal box with a window in front. The temperature of the box was kept constant by circulating, with the aid of a pump, water through the annular space of the box.

Reagents.—Merck's extra pure carbon tetrachloride and iodine were purified as in Part I of the series (*J. Indian Chem. Soc.* 1941, 18, 171). B. D. H. purest phenylacetylene and β -amylenes, further purified by distillation, and B. D. H. purest phenylpropionic acid, further purified by crystallisation, were used. Light's dicyclopentadiene and Kahlbaum's dimethylacetylene dicarboxylate were used after distillation in vacuum. It may be mentioned here that dicyclopentadiene in contact with air forms peroxides (Schulze, *J. Amer. Chem. Soc.*, 1934, 56, 1552) which affect the kinetic measurements. β -Amylene also forms peroxides in contact with air. So fresh solutions

were prepared with freshly distilled acceptors after every 2 days so that no appreciable amount of peroxides were formed to vitiate our results.

Measurement of Intensity.—The intensity of incident radiation was measured by means of a Moll galvanometer and a Moll thermopile, calibrated by means of a standard lamp supplied by the "Bureau of Standards". The energy of absorbed radiation was calculated according to the equation,

$$I_{\text{abs.}} = I_0 \times (1 - 10^{-\epsilon \cdot c \cdot d})$$

where ϵ = molecular extinction coefficient,

c = concentration of iodine in gram mols per litre, and

d = thickness of the reaction cell in cm.

The values of ϵ at different wave-lengths were found experimentally by intensity measurements in the following way. The deflections in the galvanometer were noted, first of all, with the solvent (CCl_4) alone and secondly with iodine solution in CCl_4 of known concentration. The molecular extinction coefficient (ϵ) of iodine in CCl_4 was then calculated according to the equation,

$$\epsilon = \frac{1}{c \times d} \log_{10} \frac{I_0}{I_t}$$

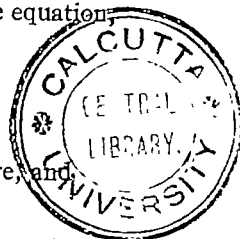
where c and d have their usual significance as mentioned before. I_0 and I_t are the incident and transmitted radiations measured. The values of ϵ for different wave-lengths (λ), e.g., 546, 436 and 366μ are recorded in Table I.

TABLE I.

$\lambda(\mu\mu)$... 366	436	546
ϵ	... 8.9	33.9	723.5

Determination of the Velocity of Reaction.—The velocity of reaction was determined by taking out 1.13 c.c. of the reaction mixture in a micro-pipette and titrating iodometrically with 0.01N-thiosulphate solution by means of a microburette.

The reactions were done at temperatures between 24° and 40° . The concentrations of iodine and the acceptor were so chosen that no measurable dark reaction was observed during the period of investigation. Dicyclopentadiene forms a precipitate with iodine solution having concentrations greater than 0.02M and so the compositions of the reaction mixtures were so chosen that the concentration of iodine was always far less than 0.02M. Iodine reacts with β -amylene even in the dark when the concentrations of the former are high. The thermal reaction was discussed in Parts I and II (*vide pp. 245, 253*).



The experimental data are recorded in Tables II to XXI. The values of k_0 , which are recorded, have been derived from the simple monomolecular equation,

$$k_0 = \frac{2.3}{t} \log_{10} \frac{a}{a-x}$$

where a , is the initial concentration of iodine in gram mols per litre and x , the concentration of the iodo product in gram mols per litre, formed in time t seconds. In other words, the reactions are all unimolecular with respect to iodine. But the quantity k_0 is not a constant, but depends on ($I_{\text{abs.}}^{\frac{1}{2}}$) and $[A]$. It is thus only a quantity to be calculated which is perhaps convenient to handle but it is not the velocity constant.

The values of k_0 were found to diminish very slightly with time. This may be due to two causes, viz., (1) there is a photostationary state, the iodo product formed gives a reverse reaction and (2) with the disappearance of iodine the absorbed energy for the same incident intensity continually diminishes. This happens only in $436\mu\mu$ and $366\mu\mu$ where ϵ is very small.

The absorbed energy may be considered to be practically constant and the iodo product formed may be regarded as negligible when the concentrations of iodine does not change by more than 10 to 15%. Hence values of k_0 as measured above may be regarded as derived under conditions of constant light absorption and negligible amount of iodo product formed.

In the sixth vertical column of Tables II to VI, are given the values of k_0 and in the 7th column are given the values of $k_0/I_{\text{abs.}}^{\frac{1}{2}}$. It will be seen from these tables that $k_0/I_{\text{abs.}}^{\frac{1}{2}}$ have always got the same value for the same monochromatic radiation, but with increase in the magnitude of the quantum absorbed by iodine, the values of $k_0/I_{\text{abs.}}^{\frac{1}{2}}$ increase.

RESULTS.

Effect of varying the Concentration of Iodine.

The notations used in the following tables are given below :

θ = temperature.

d = thickness of the reaction cell in cm.

λ = wave-length.

a, b = initial concentrations of iodine and the acceptor respectively in gram mols per litre.

I_0 = intensity of incident radiation in ergs per sq. cm. per sec.

$I_{\text{abs.}}$ = number of quanta absorbed by iodine per c.c. per sec.

ν = quantum efficiency.

TABLE II.

Acceptor=Phenylacetylene. $\theta=24^\circ$. $d=0.5$ cm.

λ	a.	b.	I_0	$I_{\text{abs.}} \times 10^{-12}$	$k_0 \times 10^4$	$k_0 \times 10^{12} / I_{\text{abs.}}^{1/2}$	γ
366 μ	0.005M	0.05M	679.2	12.54	4.3	121.5	104.0
"	0.03	"	"	63.58	10.1	126.7	248.8
"	0.005	0.1	"	12.54	8.7	245.8	210.2
436	0.005	0.05	51.0	4.01	2.3	115.5	174.7
"	0.0238	"	"	13.74	4.3	116.1	451.4
"	0.005	0.1	"	4.01	3.4	172.5	260.7
546	0.009	0.05	133.5	76.9	4.2	48.0	29.9
"	0.0225	"	"	"	"	"	75.2
"	0.01	0.1	"	"	6.8	77.5	53.6

TABLE III.

Acceptor=Dicyclopentadiene. $\theta=29^\circ$. $d=0.3$ cm.

	a.	b.	I_0	$I_{\text{abs.}} \times 10^{-12}$	$k_0 \times 10^4$	$k_0 \times 10^{12} / I_{\text{abs.}}^{1/2}$	γ
366	0.005M	0.05M	700.96	13.1	6.3	17.5	14.6
"	0.015	"	"	38.2	11.0	17.8	26.2
"	0.005	0.1	"	13.1	12.5	34.5	28.5
436	0.005	0.05	761.53	62.3	10.0	12.7	4.9
"	0.015	"	"	167.2	17.3	13.4	9.4
"	0.005	0.1	"	62.3	19.5	24.7	9.5
546	0.0049	0.05	121.15	102.15	7.5	7.4	2.2
"	0.0123	"	"	112.20	7.5	7.0	4.9
"	0.0049	0.1	"	102.5	12.7	12.5	3.7

TABLE IV.

Acceptor= β -amylene. $\theta=23^\circ$. $d=0.5$ cm.

	a.	b.	I_0	$I_{\text{abs.}} \times 10^{-12}$	$k_0 \times 10^4$	$k_0 \times 10^{12} / I_{\text{abs.}}^{1/2}$	γ
366	0.01M	0.05M	709.6	25.8	2.1	4.1	4.9
"	0.02	"	"	48.9	2.7	3.9	6.8
436	0.01	0.05	900.0	120.3	3.3	3.0	1.7
"	0.02	"	"	217.3	4.2	2.9	2.4
546	0.01	0.05	1800.0	1000.0	4.6	1.5	0.3
"	0.02	"	"	"	"	"	0.6

TABLE V.

Acceptor=Phenylpropionic acid. $\theta=30^\circ$. $d=0.5$ cm.

	a.	b.	I_0	$I_{\text{abs.}} \times 10^{-12}$	$k_0 \times 10^4$	$k_0 \times 10^{12} / I_{\text{abs.}}^{1/2}$	γ
366	0.01M	0.03M	147.1	5.4	5.4	2.3	6.2
"	0.032	"	"	15.4	8.9	2.3	11.3
436	0.01	0.03	311.5	44.7	7.0	1.0	0.9
"	0.032	"	"	98.7	10.9	1.1	2.2
546	0.01	0.03	86.5	48.1	6.1	0.9	0.8
"	0.02	"	"	"	5.6	0.8	1.4

TABLE VI.

Acceptor=Dimethylacetylene dicarboxylate. $\theta=30^\circ$. $d=0.3$ cm.

λ .	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^6$.	$k_0 \times 10^{12}/I_{\text{abs.}}^{\frac{1}{2}}$.	γ .
366 μ	0.0059M	0.125M	597.1	13.2	3.3	0.9	0.9
"	0.0339	"	"	69.6	8.1	1.0	2.4
436	0.0297	0.165	106.2	39.5	5.7	0.9	2.6
"	0.0695	"	"	63.2	7.2	0.9	4.8
546	0.0063	0.125	119.0	105.5	5.2	0.5	0.2
"	0.0252	"	"	110.8	5.1	0.5	0.7

Effect of varying the Concentration of the Acceptor.

TABLE VII.

Acceptor=Phenylacetylene. $\theta=24^\circ$. $d=0.5$ cm.

	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^4$.	γ .
366	0.01M	0.025M	679.2	24.6	3.3	81.2
"	"	0.05	"	"	6.4	158.9
"	"	0.1	"	"	11.9	295.5
"	"	0.15	"	"	17.3	429.6
436	0.015	0.025	51.0	10.04	2.6	234.0
"	"	0.05	"	"	3.7	336.3
"	"	0.1	"	"	5.3	484.5
546	"	0.033	138.46	76.9	3.8	45.5
"	"	0.066	"	"	5.1	60.3
"	"	0.132	"	"	7.5	88.7

TABLE VIII.

Acceptor=Dicyclopentadiene. $\theta=29^\circ$. $d=0.3$ cm.

	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^6$.	γ .
366	0.01M	0.25M	700.96	26.2	4.9	11.5
"	"	0.05	"	"	9.3	21.6
"	"	0.1	"	"	18.3	42.7
"	"	0.2	"	"	35.0	81.5
436	"	0.025	761.53	117.8	7.3	3.7
"	"	0.05	"	"	14.6	7.5
"	"	0.1	"	"	29.0	15.0
546	0.0123	0.0167	121.15	112.2	3.5	2.3
"	"	0.033	"	"	5.6	3.7
"	"	0.083	"	"	8.3	5.5

TABLE IX.

Acceptor = β -amylene. $\theta = 24^\circ$. $d = 0.5$ cm.

λ .	a.	b.	I_0 .	$I_{abs.} \times 10^{-13}$.	$k_a \times 10^5$.	γ .
366 μ	0.01M	0.025M	709.6	25.8	1.1	2.5
"	"	0.1	"	"	3.9	9.3
"	"	0.2	"	"	8.0	18.9
436	"	0.025	900.0	120.3	1.7	0.9
"	"	0.05	"	"	3.3	1.7
"	"	0.1	"	"	6.9	3.5
546	"	0.025	588.5	327.0	1.3	0.2
"	"	0.05	"	"	2.6	0.4
"	"	0.1	"	"	5.5	1.0

TABLE X.

Acceptor = Phenylpropionic acid. $\theta = 30^\circ$. $d = 0.5$ cm.

	a.	b.	I_0 .	$I_{abs.} \times 10^{-13}$.	$k_a \times 10^5$.	γ .
	0.01M	0.01M	147.1	5.4	1.8	2.0
"	"	0.02	"	"	3.4	3.8
"	"	0.04	"	"	7.5	8.4
436	"	0.02	311.5	44.7	5.0	0.7
"	"	0.03	"	"	7.0	0.9
"	"	0.04	"	"	9.8	1.3
546	"	0.01	86.5	48.1	2.1	0.3
"	"	0.02	"	"	4.1	0.5
"	"	0.04	"	"	8.3	1.1

TABLE XI.

Acceptor = Dimethylacetylene dicarboxylate. $\theta = 30^\circ$. $d = 0.3$ cm.

	a.	b.	I_0 .	$I_{abs.} \times 10^{-13}$.	$k_a \times 10^5$.	γ .
366	0.0115M	0.125M	597.1	25.5	4.8	1.3
"	"	0.375	"	"	14.4	3.9
436	0.0152	0.0825	318.5	69.9	3.2	0.4
"	"	0.495	"	"	21.0	2.8
546	0.0126	0.125	119.0	110.2	5.2	0.4
"	"	0.375	"	"	16.0	1.2

From Tables VII to XI it appears that velocity constant varies nearly proportionally with the concentration of the acceptor.

Effect of varying the Intensity of Absorbed Radiation.

TABLE XII.

Acceptor=Phenylacetylene. $\theta=24^\circ$. $d=0.5$ cm.

λ .	a.	b.	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^4$.	$k_0 \times 10^{12}/I_{\text{abs.}}^{\frac{1}{2}}$.	γ .
366 μ	0.01M	0.05M	24.6	6.4	129.0	158.9
"	"	"	12.3	4.5	128.6	221.7
436	0.01	0.05	7.33	3.1	114.8	256.0
"	"	"	2.44	1.8	115.4	446.7
546	0.015	0.05	76.9	4.2	48.0	49.7
"	"	"	29.0	2.7	49.6	83.7

TABLE XIII.

Acceptor=Dicyclopentadiene. $\theta=29^\circ$. $d=0.3$ cm.

	a.	b.	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^6$.	$k_0 \times 10^{12}/I_{\text{abs.}}^{\frac{1}{2}}$.	γ .
366	0.01M	0.1M	26.2	18.3	35.7	42.3
"	"	"	4.5	7.7	36.2	103.0
436	0.01	0.1	96.3	25.0	25.5	15.7
"	"	"	10.7	8.3	25.5	47.2
546	0.0099	0.1	112.2	12.8	12.1	6.8
"	"	"	56.1	9.3	12.4	9.9

TABLE XIV.

Acceptor= β -amylene. $\theta=24^\circ$. $d=0.5$ cm.

	a.	b.	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^6$.	$k_0 \times 10^{12}/I_{\text{abs.}}^{\frac{1}{2}}$.	γ .
366	0.01M	0.1M	25.8	3.9	9.5	9.3
"	"	"	6.5	2.1	9.6	19.3
436	0.01	0.1	120.3	6.9	6.3	3.5
"	"	"	6.7	1.7	6.5	15.3
546	0.01	0.1	327.0	5.6	3.1	1.0
"	"	"	24.1	1.5	3.1	3.8

TABLE XV.

Acceptor=Phenylpropionic acid. $\theta=30^\circ$. $d=0.5$ cm.

	a.	b.	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^6$.	$k_0 \times 10^{12}/I_{\text{abs.}}^{\frac{1}{2}}$.	γ .
366	0.01M	0.03M	5.4	5.4	2.3	6.2
"	"	"	2.2	3.9	2.6	10.9
436	0.01	0.03	44.7	7.0	1.0	1.0
"	"	"	13.9	3.8	1.0	1.7
546	0.01	0.03	48.1	6.0	0.9	0.8
"	"	"	24.0	4.2	0.9	1.1

- TABLE XVI.

Acceptor = Dimethylacetylene dicarboxylate. $\theta = 30^\circ$. $d = 0.3$ cm.

λ .	a .	b .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^0$.	$k_0 \times 10^{12} / I_{\text{abs.}}^{1/2}$.	γ .
366 μ	0.0115M	0.125M	25.5	4.8	1.0	1.3
"	"	"	12.7	3.5	1.0	1.9
436	0.015	0.165	69.9	6.9	0.8	0.9
"	"	"	23.4	4.0	0.8	1.5
546	0.0126	0.125	110.2	5.2	0.5	0.4
"	"	"	55.1	3.7	0.5	0.5

From Tables XII to XVI the velocity constant appears to be directly proportional to the square root of the intensity of absorbed radiation.

Effect of Varying the Temperature

TABLE XVII.

Acceptor = Phenylacetylene. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^4$		v .
					$\theta = 24^\circ$.	$\theta = 34^\circ$.	
366 μ	0.01M	0.05M	679.2	24.6	6.4	6.5	1.01
436	"	"	51.0	7.3	2.9	3.1	1.07
546	0.015	0.066	138.5	76.9	5.1	5.7	1.1

TABLE XVIII.

Acceptor = Dicyclopentadiene. $d = 0.3$ cm.

λ .	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^5$		v .
					$\theta = 29^\circ$.	$\theta = 39^\circ$.	
366	0.01M	0.1M	700.96	26.2	18.3	18.3	1.0
436	"	0.05	747.2	117.8	14.6	15.2	1.04
546	0.0099	0.05	121.15	112.2	7.4	8.4	1.13

TABLE XIX

Acceptor = β -amylene. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{\text{abs.}} \times 10^{-12}$.	$k_0 \times 10^5$		v .
					$\theta = 24^\circ$.	$\theta = 34^\circ$.	
366	0.01M	0.05M	709.6	25.8	2.1	2.1	1.0
436	"	"	900.0	120.3	3.3	3.4	1.03
436	"	"	43.3	24.1	0.8	0.9	1.12

TABLE XX.

Acceptor = Phenylpropionic acid. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{abs.} \times 10^{-12}$.	$k_8 \times 10^6$		v .
					$\theta = 24^\circ$.	$\theta = 34^\circ$.	
366 μ	0.01M	0.03M	147.1	5.4	5.4	5.4	1.0
436	"	"	311.5	44.7	7.0	7.2	1.03
546	"	"	86.5	48.1	6.1	6.6	1.00

TABLE XXI.

Acceptor = Dimethylacetylene dicarboxylate. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{abs.} \times 10^{-12}$.	$k_8 \times 10^6$		v .
					$\theta = 30^\circ$.	$\theta = 40^\circ$.	
366	0.0223M	0.125M	597.1	47.2	6.7	6.9	1.03
436	0.0152	0.165	318.5	69.9	6.9	7.3	1.05
546	0.0126	0.126	119.0	110.2	5.2	5.5	1.07

 v = Temperature coefficient for 10° rise.

From Tables XVII to XXI we see that the temperature coefficient is nearly unity.

Quantum Efficiency of the Process.

Calculation of the quantum efficiency has not much theoretical significance in these reactions, because the velocity observed is really due to reaction chains started by the iodine atoms which attain a definite value at the stationary state. However, the quantum efficiency has been calculated here only to have some idea of the mechanism of the reaction.

A typical method of calculation is given below:—

At the beginning of the reaction we may take it that the reaction is represented by the equation

$$\Delta x = k_6 [I_2] \Delta t.$$

The significance of this equation will be found from the discussion.

Taking the concentration of phenylacetylene = 0.1M; the concentration of iodine = 0.01M and $k_8 = 6.8 \times 10^{-4}$, and $\lambda = 546\mu$,

we get $\frac{\Delta x}{\Delta t} = k_6 [I_2] = 6.8 \times 10^{-4} \times 0.01 \times 10^{-3}$ mols per c.c. per sec.

$$= 6.8 \times 10^{-4} \times 0.01 \times 10^{-3} \times 6.06 \times 10^{23} \text{ molecules of iodine per c.c. per sec.}$$

$$= 41.208 \times 10^{14} \text{ molecules of iodine per c.c. per sec.}$$

Again, when the intensity of incident radiation = 138.5 ergs per sq. cm. per sec. and the thickness of the cell = 0.5 cm., the intensity of absorbed radiation = 277.0 ergs per c.c. per sec.

Therefore, the number of quanta absorbed by 1 c.c. of solution per sec.

$$(I_{\text{abs.}}) = \frac{277.0}{h\nu} = \frac{277.0}{3.6 \times 10^{-12}} = 76.9 \times 10^{12}$$

$$\text{Hence } \gamma = \text{quantum efficiency} = \frac{41.208 \times 10^{14}}{76.9 \times 10^{12}} = 53.6.$$

All the other calculations are made in the same way.

DISCUSSION.

The reactions have the following characteristics.—

1. They are unimolecular with respect to iodine. Of course, it is quite wrong in photochemical reactions to search for velocity constants of the first, second or any order. The quantity k_6 which has been calculated according to the equation,

$$k_6 = \frac{2.3}{t} \log_{10} \frac{a}{a-x}$$

is not a constant, but depends on $I_{\text{abs.}}^{\frac{1}{2}}$ and on $[A]$. It is thus only a quantity to be calculated which is perhaps convenient to handle but it is not the velocity constant.

2. The quantity k_6 diminishes slightly with the progress of the reaction, and is directly proportional to the square root of the intensity of the absorbed radiation. It increases nearly proportionally with the increase in the concentration of the acceptors. At 546 $\mu\mu$, where the absorption of iodine is complete with very dilute solutions, k_6 is independent of the initial concentrations of iodine. At 436 and 366 $\mu\mu$, where iodine has weak absorption, k_6 increases with increasing concentration of iodine. In fact $k_6 \times 10^{12} / I_{\text{abs.}}^{\frac{1}{2}}$ remains always constant for a particular wave-length but increases with the increase in the magnitude of the quanta absorbed by iodine.

The temperature coefficient is small, nearly unity. The quantum efficiency is very high in the case of phenylacetylene and dicyclopentadiene, but in other cases it is very small.

The experimental data recorded above can be explained by the following addition reactions :



where A represents the acceptor molecule. In these reactions the concentration of iodine atoms per c.c. in the stationary state is given by the relation

$$[\text{I}] = \left(\frac{\text{I}}{k_2} \cdot I_{\text{abs}} \right)^{\frac{1}{2}}$$

where I_{abs} = number of quanta absorbed by iodine per c.c. per sec. Hence the above mechanism given for

$$\begin{aligned}
 k_6 &= - \frac{\text{I}}{[\text{I}_2]} \cdot \frac{d[\text{I}_2]}{dt} = k_5 \cdot \frac{k_3}{k_4} \left(\frac{\text{I}}{k_2} \cdot I_{\text{abs}} \right)^{\frac{1}{2}} [\text{A}] \\
 &= k' (I_{\text{abs}})^{\frac{1}{2}} [\text{A}] \quad \dots (a)
 \end{aligned}$$

The equation (a) agrees very well with the experimental observations recorded in Tables XII to XVI that k_6 varies directly as the square root of the energy of absorbed radiation.

From equation (a) it also follows that k_6 is directly proportional to the concentration of the acceptor, which has been approximately found to be the case.

In conclusion the author takes this opportunity to offer his sincere thanks to Dr. J. C. Ghosh D.Sc. for his suggestions and kind interest in the work.

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Received February 3, 1941.

IODINATION. PART V. STUDIES ON THE PHOTOIODINATION OF PHENYLACETYLENE IN LIGHT OF DIFFERENT FREQUENCIES IN POLAR SOLVENT.

BY S. K. BHATTACHARYA.

The kinetics and mechanism of the iodination of phenylacetylene in alcoholic solution in radiations of frequencies 366, 436 and 546 μ have been studied. Results indicate that the reaction, which is unimolecular in nature, is reversible and does not proceed to completion. The temperature coefficient of the reaction is small as also the quantum efficiency.

Instances of photochemical iodination of unsaturated organic compounds in polar solvents, like alcohol, etc., are not at all found in the literature. The object of the present investigation is to study in detail the kinetics and mechanism of the iodination of phenylacetylene in alcoholic solution in light of frequencies 366, 436 and 546 μ . The reaction is a reversible one and does not go to completion.

The experimental procedure and arrangement have been described in the previous parts.

Merck's purest absolute alcohol was further purified by distillation over metallic calcium before use. The reaction between iodine and phenylacetylene in solution of CCl_4 does not proceed in the dark even with high initial concentrations of iodine but in alcoholic solution there is an appreciable dark reaction with high initial concentrations of iodine which has been studied in Part III of the series (*vide p.* 253). In this investigation the composition of the reaction mixtures were so chosen that there was no dark reaction during the period of investigation.

Measurement of Intensity and Extinction Coefficient of Iodine in Alcoholic Solution.

The intensity of incident radiation was measured by means of a Moll thermopile and a Moll galvanometer as described in Part IV of the series (*vide p.* 257).

The energy of absorbed radiation was calculated according to the equation

$$I_{\text{abs.}} = I_0 (1 - 10^{-\epsilon \cdot c \cdot d}).$$

where $I_{\text{abs.}}$, I_0 , ϵ , c and d have their usual significance as described in Part IV. The extinction coefficient (ϵ) of iodine in alcoholic solution was determined in different wave-lengths (λ) in exactly the same way as has been described in Part IV. The values of ϵ of iodine in alcoholic solution are recorded in Table I.

TABLE I.

$\lambda(\mu\mu)$...	546	436	366
ϵ	..	106.2	3742.0	5322.5

The experimental data are recorded in Tables II to V. The values of k_6 have been derived from the simple monomolecular equation,

$$k_6 = \frac{2.3}{t} \log_{10} \frac{a}{a-x}$$

where a is the initial concentration of iodine and x , the concentration of the iodo-product in gram mols per litre formed in time t seconds.

The values of k_6 were found to diminish slightly with time. The absorbed energy may be considered to be practically constant and the iodo product formed may be regarded as negligible when the concentrations of iodine do not change by more than 10%. Hence values of k_6 , as measured above, may be regarded as derived under conditions of constant light absorption and negligible concentration of the iodo product formed.

In the sixth vertical column of Tables II and IV are given the values of k_6 and in the 7th vertical column are given the values of $k_6/I_{\text{abs}}^{\frac{1}{2}}$. It will be seen that $k_6/I_{\text{abs}}^{\frac{1}{2}}$ have always got the same value for the same monochromatic radiation.

R E S U L T S.

The effect of varying the concentrations of iodine on the velocity of reaction is shown in Table II.

λ = wave-length; a , b = initial concentrations of iodine and phenyl acetylene in gram mols per litre.

I_0 = intensity of incident radiation in ergs per sq. cm. per sec.

I_{abs} = number of quanta absorbed per c.c. per sec.

γ = quantum efficiency.

θ = temperature.

d = thickness of the cell.

TABLE II.

$\theta = 25^\circ$.

$d = 0.5$ cm.

λ	a	b	I_0	I_{abs}	k_6	$k_6/I_{\text{abs}}^{\frac{1}{2}}$	γ
366 μ	0.0077M	0.111M	182.5	68.1×10^{12}	7.43×10^{-6}	0.90×10^{-12}	0.51
"	0.0157	"	"	"	7.43	0.90	1.04
"	0.0248	"	"	"	7.43	0.90	1.64
436	0.00765	0.055	628.3	279.2	7.31	0.44	0.12
"	0.0155	"	"	"	7.33	0.44	0.25
"	0.0232	"	"	"	7.30	0.44	0.37
"	0.00765	0.111	"	"	14.97	0.90	0.25
"	0.0153	"	"	"	14.67	0.88	0.49
"	0.0135	"	"	"	14.71	0.88	0.62
546	0.0078	0.111	144.3	49.2	7.00	1.00	0.67
"	0.0159	"	"	69.8	8.11	0.97	1.11
"	0.0252	"	"	76.5	8.50	0.97	1.69

From this table we see that $k_b \times 10^{12} / I_{abs.}^{\frac{1}{2}}$ is nearly independent of the initial concentration of iodine as well as of the wave-lengths used.

The effect of varying the concentration of the acceptor on the velocity of reaction is shown in Table III.

TABLE III.

$\theta = 25^\circ$. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{abs.}$	k_b .	γ .
366 μ	0.0077M	0.055M	182.5	68.1×10^{12}	3.75×10^{-6}	0.26
"	"	0.111	"	"	7.43	0.51
"	"	0.167	"	"	11.28	0.77
436	0.00765	0.055	628.3	279.2	7.31	0.12
"	"	0.111	"	"	14.97	0.25
"	"	0.167	"	"	24.83	0.41
546	0.0078	0.055	144.3	49.2	4.27	0.41
"	"	0.111	"	"	7.0	0.67
"	"	0.167	"	"	12.1	1.15

From this table we see that the velocity constant is directly proportional to the concentration of the acceptor.

The effect of varying the intensity on the velocity of reaction is shown in Table IV.

TABLE IV.

$\theta = 25^\circ$. $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{abs.}$	k_b .	$k_b / I_{abs.}^{\frac{1}{2}}$	γ .
366 μ	0.0157M	0.111M	182.5	68.1×10^{12}	7.43×10^{-6}	0.90×10^{-12}	1.04
"	"	"	91.3	34.1	5.03	0.86	1.40
436	0.0153	0.111	628.3	279.2	14.67	0.88	0.49
"	"	"	169.8	75.5	7.91	0.91	0.97
546	0.0159	0.111	144.3	69.8	8.11	0.97	1.11
"	"	"	72.2	34.1	5.74	0.98	1.62

From this table we see that the velocity constant is directly proportional to the square root of absorbed radiation.

The effect of varying the temperature on the velocity of reaction is shown in Table V.

TABLE V

 $d = 0.5$ cm.

λ .	a .	b .	I_0 .	$I_{\text{abs.}}$	$k_6 \times 10^4$.		v .
					$\theta = 25^\circ$	$\theta = 35^\circ$	
366 $\mu\mu$	0.0077M	0.111M	182.5	68.1×10^{12}	7.43	7.5	1.01
436	0.00765	„	628.3	279.2	14.97	16.8	1.12
546	0.0073	„	70.0	33.0	5.45	6.21	1.14

v = the temperature coefficient for 10° rise.

From this table we see that the temperature coefficient is nearly unity.

DISCUSSION.

The reaction has the following characteristics :—

The reaction is unimolecular with respect to iodine. The quantity k_6 which diminishes slightly with the progress of the reaction, is directly proportional to the square root of the intensity of the absorbed radiation, and increases proportionally with the increase in the concentration of the acceptor in all the three wave-lengths used. It also increases with increasing concentration of iodine at 546 $\mu\mu$ where the absorption is weak but remains constant at 436 and 366 $\mu\mu$ where the absorption is very strong. In fact $k_6 \cdot 10^{12} / I_{\text{abs.}}^{1/2}$ is independent of the initial concentration of iodine and also of the three wave-lengths used in this investigation. The temperature coefficient is small, nearly unity, and the quantum efficiency is also small.

The mechanism of the reaction is the same as has been proposed in Part IV.

It has been shown in Part IV that the quantum efficiency of the photoiodination of phenylacetylene in solution of CCl_4 is very high, whereas in the present investigation it is very low. This difference in the values of the quantum efficiency indicates that the reaction has got a long chain in non-polar solvent but in polar solvent the chain length is greatly diminished.

In conclusion the author takes this opportunity to offer his sincere thanks to Dr. J. C. Ghosh, D.Sc. for his suggestions and advice.

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Received February 3, 1941.

THE DETECTION AND DETERMINATION OF PYRIDINE BASES IN DENATURED SPIRIT.

By H. D. SURI, GURCHARAN SINGH AHLUWALIA AND H. B. DUNNICLIFF.

Three methods have been described for the detection and determination of pyridine bases in denatured spirit depending upon the use of 6% CdCl_2 solution, titration with H_2SO_4 with congo-red as an external indicator and colorimetric experiments with the use of cyanogen bromide-aniline reagent.

Spirit is ordinarily denatured in India by the addition of 0.5% light caoutchoucine and 0.5% pyridine bases of guaranteed mineral origin. The "pyridine bases" or commercial 90/160 pyridine is a tall product conforming to the Government of India specifications and consisting principally of pyridine, picolines, lutidines and collidines.

In the examination of denatured spirits, the amounts of light caoutchoucine and pyridine bases present have to be determined. This paper deals only with the pyridine bases, the estimation of which is difficult owing to their variable composition and describes the most efficient procedure for their identification and determination in denatured spirit. The three methods for determining pyridine bases are given below.

Volumetric Method.

Aqueous solutions of pyridine can be estimated volumetrically by titration with standard sulphuric acid using methyl orange, bromophenol blue or congo-red paper (as an external indicator) provided ammonia and caustic alkalis are absent. Bromophenol blue cannot be used for titrating alcoholic solutions of pyridine. When the presence of ammonia or caustic alkalis is suspected (detected by the use of red litmus paper or phenolphthalein, on which pyridine has practically no effect) the solution is exactly neutralised with $N/10$ -sulphuric acid (phenolphthalein) and then titrated for pyridine against $N/10$ -sulphuric acid using any one of the above-mentioned indicators.

To eliminate alcohol and substances such as caustic alkalis or non-volatile alkaloidal bases, which interfere in the titration with sulphuric acid, the following distillation method has been worked out.

Distillation Method.—Measure 100 ml. of the sample of denatured spirit under test into a Thorpe's revenue still and just acidify (congo-red paper)

with dilute sulphuric acid and distil until about 3 ml. of residue remain. Cool the distillation flask, add 100 ml. of distilled water and make the solution alkaline (litmus) with dilute sodium hydroxide solution, adding a few drops in excess. If pyridine is present, even in traces, its characteristic odour will be perceptible. Connect the flask again to the distillation apparatus and collect about 100 ml. of the distillate in a graduated flask making the volume up to 100 ml. with distilled water. The distillate should be neutral to phenolphthalein (ammonia absent). Titrate 10 ml. of the distillate with $N/10\text{-H}_2\text{SO}_4$ using bromophenol blue or methyl orange as internal, or congo-red paper as an external indicator. The volume of $N/10\text{-H}_2\text{SO}_4$ required should not be less than 4.7 ml. This limit is based on a number of determinations on spirit denatured with pyridine bases which conformed to the Government of India specifications.

Precipitation Method.

Pyridine bases in aqueous solution resemble alkaloids in giving distinct precipitates with mercuric chloride, cadmium chloride, iodine in potassium iodide solution (Harvey and Sparks, *J. Soc. Chem. Ind.*, 1918, **87**, 41T), phosphotungstic acid, silicotungstic acid, Dragendorff's reagent (Pavolini, *Chim. Ind. Agr. Boli.*, 1931, **6**, 272) and Nessler's reagent.

Preliminary tests showed that, of these reagents, cadmium chloride is the only one suitable for estimating pyridine bases in 0.5% alcoholic solution. The others either do not give any precipitate in the presence of much alcohol, or, if a precipitate forms, it only appears after long standing.

Ionescu and Slusanchi (*Bull. soc. chim.*, 1933, **53**, 1087) claim that the sensitiveness of the cadmium chloride reaction is proportional to the amount of reagent added, more particularly if sodium chloride is also present. They describe a method for the estimation of pyridine by measuring the time taken for a noticeable precipitate to appear when $N\text{-CdCl}_2$ in $N\text{-NaCl}$ is added to an aqueous solution of pyridine bases. The authors found that this reagent gave a well defined crystalline precipitate with alcoholic solutions of pyridine, though the reaction was somewhat delayed owing to the presence of alcohol. Hence, it cannot be applied for the estimation of pyridine bases in denatured spirit.

It was found, however, that by taking a larger quantity of the 6% aqueous solution of cadmium chloride than that prescribed in the official test (0.5 c.c.), the characteristic precipitate is obtained immediately.

The following qualitative test for the detection of pyridine bases is therefore proposed for rapid work.

Procedure.—Of the sample of denatured spirit, 15 ml. are shaken vigorously in a 25 ml. stoppered measuring cylinder with 3 ml. of a 6% solution of cadmium chloride ($\text{CdCl}_2, 2\text{H}_2\text{O}$). A characteristic white crystalline precipitate forms immediately which has no tendency to settle down on standing. It is advisable to cool the solution to about 20° though it has been observed that the test is valid up to about 37° .

Colorimetric Method.

Cyanogen bromide and aniline (Lehner, *Chem. Ztg.*, 1922, **46**, 877; Goris and Larsonneau, *Bull. sci. pharmacol.*, 1922, **28**, 497), copper sulphate and ammonium thiocyanate (Spacu, *Z. anal. Chem.*, 1925, **67**, 31), 2:4-dinitrochlorobenzene (Von Gerichten, *Ber.*, 1899, **32**, 2571), benzenesulphonyl chloride and 2:3-diaminophenazine hydrochloride (Pavolini, *Industria Chimica*, 1932, **8**, 692) give characteristic colours in dilute solutions containing pyridine.

Cyanogen bromide forms a yellow coloured compound with pyridine and the reaction is sensitive to one part of pyridine in about 350,000 parts of water (Tallantyre, *J. Soc. Chem. Ind.*, 1930, **49**, 466r). After removing alcohol and caoutchoucine, this method can be employed to determine pyridine bases in denatured spirit using the following procedure, all details of which should be meticulously observed.

Cyanogen Bromide Test.

(i) *Cyanogen Bromide Solution*—Take 1 ml. of bromine in 100 ml. of distilled water, cool in ice and add from a burette, drop by drop, 5% solution of potassium cyanide until the colour of bromine just disappears (about 25-26 ml.). The solution prepared under these conditions has no colour (due to excess of bromine) and is not alkaline to litmus. Excess of alkali vitiates the test and should be carefully neutralised with $N/10\text{-H}_2\text{SO}_4$. This reagent keeps well for six days but after that it decreases in its sensitiveness and should not be used.

(ii) *Saturated Solution of Aniline.*—Shake 5 ml. of freshly distilled aniline in 100 ml. of distilled water for 15 minutes and filter the supernatant liquor.

(iii) *Standard Solution of Pyridine Bases.*—Dissolve 0.5 ml. of pyridine bases satisfying the specifications laid down by the Government of India

in 40 ml. of distilled water. Neutralise exactly with $N/2\text{-H}_2\text{SO}_4$ (congo-red paper) and make up the volume to 100 ml. This control solution should be freshly prepared.

Method.—Take 10 ml. of denatured spirit under test in a basin, make it just acid (congo-red paper) with $N/10\text{-H}_2\text{SO}_4$ and evaporate on a water-bath until about 2-3 ml. remain. Add 5 ml. of distilled water to the residue and evaporate almost to dryness. Add about 20 ml. of distilled water and filter washing the basin and the filter thrice with 5 ml. of distilled water. Exactly neutralise (congo-red paper) with $N/10\text{-NaOH}$ and make up to 50 ml. Take 5 ml. of this solution in a Nessler's tube (50 ml. capacity), add 1 ml. of aniline solution and make up to 50 ml.

Simultaneously prepare a series of standard comparison tubes, each containing different volumes of the standard pyridine solution (solution iii), ranging from 0.1 to 0.01% pyridine. Cool all the test solutions to 20° , and introduce 2 ml. of cyanogen bromide solution from a burette into each of the tubes. Allow to stand for 10 minutes, stirring the solution occasionally with a glass rod and compare the yellow colour produced.

If the requisite quantity of pyridine has been added to the spirit, the colour produced in the tube containing the test solution should match that given by 5 ml. of 0.1% standard solution. The yellow colour gradually changes to orange on keeping for longer periods.

ON THE STUDY OF THE DEHYDRATION OF SOME PURE AND MIXED CHROMI-SELENIC ALUMS AND THE FORMATION OF CORRESPONDING COMPLEX CHROMI-SELENATES.

BY PRODOSH CHANDRA RAYCHOUDEHURY.

The changes of properties of some pure and mixed chromi-selenic alums with rise of temperature have been studied. In the vacuum desiccators and in the room temperature, different hydrates are formed. But at higher temperatures up to 160° , the violet alums are converted into green complex chromi-selenates in which the Cr, SeO₄ and SO₄ ions are absent.

The properties of the chromo-sulphuric alums at higher temperatures have been studied by many investigators (Müller-Erbach, *Z. physikal. Chem.*, 1888, **2**, 113; Lescoeur and Mathurin, *Bull. soc. chim.*, 1888, **50**, 33; Lowel, *Ann. chim. phys.*, 1855, *iii*, **44**, 320).

At the ordinary temperatures chromo-alums over concentrated H₂SO₄ lose six molecules of water. Above 80° to 90° further molecules of water are eliminated accompanied by change of colour from violet to green. At higher temperatures, anhydrous products are also obtained. Using the Tensi-eudiometric method of Huttig (*Z. anorg. Chem.*, 1920, **114**, 162; 1922, **121**, 245; 1922, **122**, 46; 1923, **126**, 168), Krauss, Fricke and Queren-gasser (*Z. anorg. Chem.*, 1929, **181**, 38) found potassium chromium alum to exist above 21° as a dodecahydrate. At 95° it again changed into tetrahydrate and became anhydrous above 408° , whereas the corresponding aluminium salt existed as 6-, 4-, 2-, and 0- hydrates at temperatures above 47° , 80° , 120° and 240° respectively.

Fabre prepared chromo-selenic alums by mixing violet chromium selenate with selenates of Na, K, Rb, Cs, Tl, etc. (*Compt. rend.*, 1887, **105**). The alums form very distinct octahedra. They are violet-red by transmitted light and their solutions are violet when cold but at 55° - 60° become green. The solutions crystallise only when allowed to evaporate spontaneously for several months. The selenic alums are more soluble than the corresponding sulphuric alums. Gerichten (*Bei.*, 1873, **6**, 162) also prepared many chromi-selenic alums. Recently Sarkar and Bhattacharyya prepared a mixed chromo-selenic alum which formed violet octahedral crystals (*J. Indian Chem. Soc.*, 1930, **7**, 765).

In this paper, the changes of properties of the following alums with rise of temperature have been studied. The alums were prepared according to the methods given in the respective papers.

- I. $\text{Cr}_2(\text{SeO}_4)_3 \cdot (\text{NH}_4)_2 \text{SeO}_4, 24\text{H}_2\text{O}$.
- II. $\text{Cr}_2(\text{SeO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4, 24\text{H}_2\text{O}$.
- III. $\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SeO}_4, 24\text{H}_2\text{O}$.
- IV. $\text{Cr}_2(\text{SeO}_4)_3 \cdot \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}$ (Gerichten, *loc. cit.*).
- V. $\text{Cr}_2(\text{SeO}_4)_3 \cdot \text{Na}_2 \text{SeO}_4, 24\text{H}_2\text{O}$ (Fabre, *loc. cit.*).
- VI. $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2 \text{SeO}_4, 24\text{H}_2\text{O}$ (Sarkar and Bhattacharyya, *loc. cit.*).

Since the selenates are decomposed at higher temperatures, the anhydrous products could not be obtained as in the case of the chromo-sulphuric alums. But at the room temperature (26° - 27°) and in the vacuum desiccator the hydrates with 11, 11, 12, 12, 10 and 11 H_2O respectively were obtained from the above mentioned alums.

The following is a list of the complex hydrates described for the first time in this paper.

- (A) $(\text{NH}_4)_2 [\text{Cr}(\text{SeO}_4)_2], 2 \cdot 5 \text{H}_2\text{O}$.
- (B) $(\text{NH}_4)_2 \left[\text{Cr} \begin{array}{c} (\text{SeO}_4)_3 \\ (\text{SO}_4) \end{array} \right], 3 \text{H}_2\text{O} \text{ and } 1 \cdot 5 \text{H}_2\text{O}$.
- (C) $(\text{NH}_4)_2 \left[\text{Cr} \begin{array}{c} (\text{SeO}_4) \\ (\text{SO}_4)_3 \end{array} \right], 4\text{H}_2\text{O}, 3 \cdot 5 \text{H}_2\text{O}, 3 \text{H}_2\text{O} \text{ and } 2 \cdot 5 \text{H}_2\text{O}$.
- (D) $\text{Na}_2 [\text{Cr}(\text{SeO}_4)_4], 2\text{H}_2\text{O}, \text{H}_2\text{O} \text{ and } 0 \cdot 5 \text{H}_2\text{O}$.
- (E) $\text{Na}_2 \left[\text{Cr} \begin{array}{c} (\text{SeO}_4) \\ (\text{SO}_4)_3 \end{array} \right], 4 \text{H}_2\text{O}, 3\text{H}_2\text{O} \text{ and } 2 \text{H}_2\text{O}$.

EXPERIMENTAL.

Known weights of the violet alums were left in desiccators over H_2SO_4 and after two or three days, they were found to lose in weight which was due to loss of water. The partially dehydrated salt was then left in a vacuum desiccator, when there was no loss in weight even after 48 hours.

The colour of the alums remained violet; Cr , SeO_4 or SO_4 ions could be detected in aqueous solutions.

The alums were then heated in a regulated air thermostat at various temperatures for many hours and the loss in weight determined for each temperature. The results of dehydration of the salts studied in this paper are shown in Table I. The results are shown in the curves (Figs. 1-3).

TABLE I.

	Dehydration temperatures.											
	26°	80°	85°	90°	100°	105°	110°	120°	130°	140°	150°	160°
	vacuum											
Salt I	20'03	20'98	20'98	22'2	26'7	29'0	30'3	30'3	30'3	30'3	30'3	30'3
Salt II	20'7	33'1	33'1	34'3	34'3	34'3	36'97	36'97	36'97	36'97	36'97	36'97
Salt III	22'1	35'9	36'5	36'5	36'5	36'5	37'1	37'1	37'7	37'7	38'5	38'5
Salt IV	19'09	31'5	31'9	31'9	31'9	31'9	32'9	32'9	33'6	35'5	35'5	35'5
Salt V	21'6	33'5	34'2	34'2	34'2	34'2	35'5	35'5	36'2	36'8	36'8	36'8
Salt VI	22'2	36'1	36'1	37'2	37'2	37'2	38'1	39'1	39'1	39'1	39'1	39'1

FIG. 1.

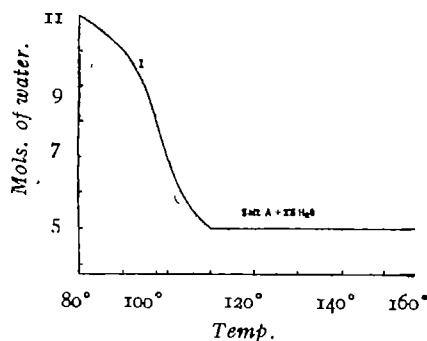
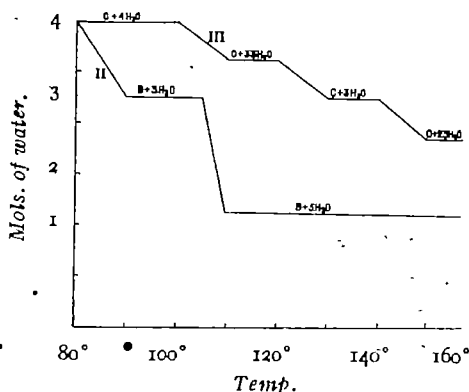


FIG. 2.



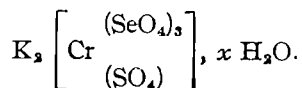
DISCUSSION.

In the case of salt I, 19 molecules of water were eliminated between 80° and 110°. The violet alum turned perfectly green and when dissolved in ice-cold water formed a green solution in which both Cr and SeO_4 ions were not detected. But if the solution was heated, the complex decomposed. As there was no loss in weight from 110° to 160°, a new complex (A), stable between large range of temperatures, was formed.

Between 90° and 105°, 21 molecules of water were removed from the salt II and green hygroscopic powder was obtained. The salt formed with water a green solution in which Cr, SeO_4 and SO_4 ions were absent in the cold. So a definite complex hydrate with 3 H_2O was formed. After removal of 22.5 molecules of water at 110°, the green product obtained was sparingly soluble in water forming a green solution in which the Cr, SeO_4 and SO_4 ions were absent. Thus another definite complex hydrate (B) with 1.5 molecules of water and stable up to 160° was obtained.

On heating, the salt III was converted into four different hydrates of a complex (C) with 4, 3.5, 3 and 2.5 molecules of H_2O , with stability range of 80°-100°, 110°-120°, 130°-150°, 150°-180° respectively. Cr, SO_4 , and SeO_4 ions were absent in the complex in the cold.

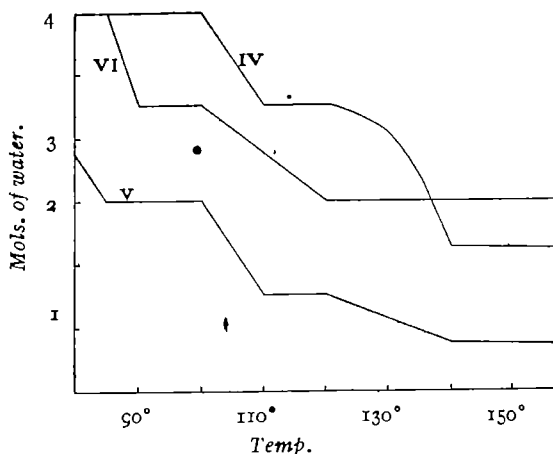
The Salt IV, was, on heating, converted into three definite perfectly green complex hydrates, having 4, 3 and 1.5 molecules of water, stable between the temperatures 80° and 100°; 100° and 120°; 130° and 160° and having the composition



The three definite complex hydrates (D) having 2, 1 or 0.5 molecules of water were produced from the salt V. Cr and SeO_4 ions were absent in the cold.

FIG. 3.

Dehydration curves of salts IV, V & VI.



The salt VI on heating formed a hygroscopic powder. The green aqueous solution gave no test for Cr, SeO_4 and SO_4 ions. Thus three definite complex hydrates (E) having 4, 3 or 2 molecules of water and stable between 80° and 85° , 90° and 100° and 120° and 160° were obtained.

All these 16 compounds were definite green coloured hydrates as was shown by their stability between large ranges of temperatures. They were all complexes; Cr, SeO_4 or SO_4 ions were not identified in freshly prepared cold aqueous solutions. They were not, however, stable being decomposed on standing or on heating.

The author's thanks are due to Dr. P. B. Sarkar for kindly suggesting this work and also for all the facilities in his laboratory.

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Received December 3, 1940.

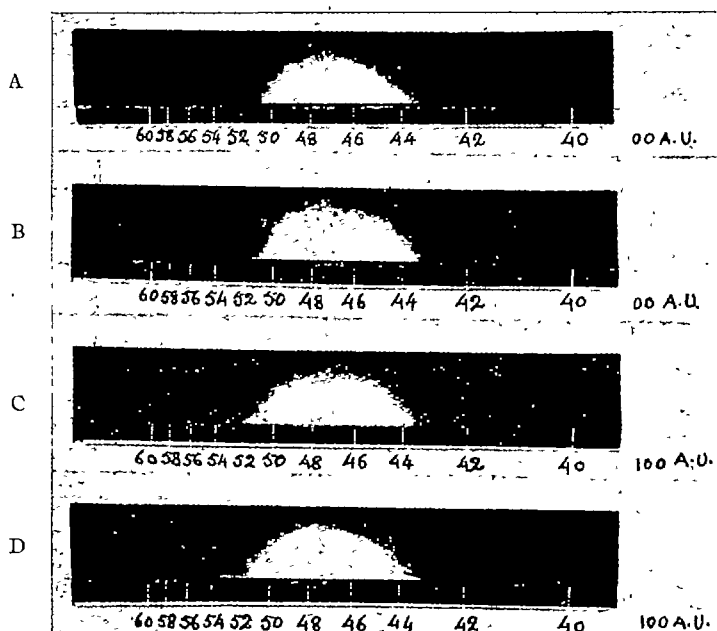
THE SENSITISATION SPECTRA OF CERTAIN CYANINE DYES DERIVED FROM α -PICOLINE.

By M. Q. DOJA.

The sensitiation spectra of the methochloride, the methobromide and the methiodide of 2-*p*-dimethylaminostyrylpyridine have been photographed and the relative sensitising power of these compounds compared.

With a view to examine the influence of change of anion on the properties of cyanine dyes the methochloride, the methobromide and the methiodide of 2-*p*-dimethylaminostyrylpyridine were prepared (Doja, *J. Indian Chem. Soc.*, 1940, 17, 347). The relative sensitising power of these dyes for photographic plates has now been examined and reported in this paper. The spectrographs given in Fig. 1 show that the chloride (No. B) does not appreciably increase the range of sensitisation, except a little towards the violet, but enhances the intensity of sensitisation. The

Fig. 1.

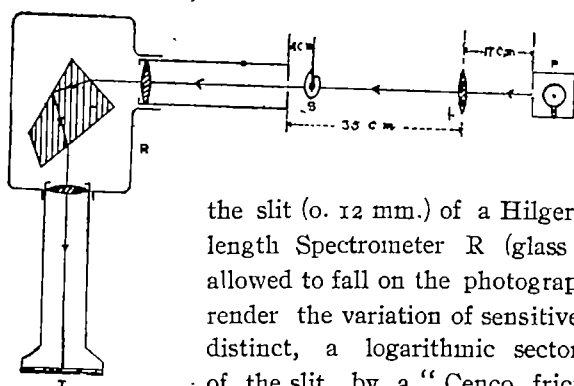


A-D refer respectively to unbathed plate, chloride, bromide and iodide.

bromide (No. C), in addition to the extra-sensitisation towards the violet, extends the sensitisation on the other side, to about λ 5600 in the green-yellow. The iodide (No. D) maintains the additional sensitisation in the violet, but extends the sensitisation in the yellow still further to about λ 5700.

The photographs were taken on Ilford Process plates. These were bathed for three minutes in solution of the dyestuffs (1:50,000 in rectified spirit), dried by means of an electric fan, and exposed for $1\frac{1}{2}$ minutes to a white light spectrum produced in the following manner :—

FIG. 2.



Light from a 100 c.p.
"pointolite" lamp P
(Fig. 2) was passed
through a lens L into

the slit (0.12 mm.) of a Hilger's constant deviation wavelength Spectrometer R (glass prism, $n=1.74$), and then allowed to fall on the photographic plate T. In order to render the variation of sensitiveness with wave-length more distinct, a logarithmic sector S, was rotated in front of the slit, by a "Cenco friction drive speed control", at about 60 revolutions per minute. The reference scale

was set up by photographing the helium and mercury lines on the plates with the help of the usual auxiliary comparison prism.

I wish to express my thanks to Professor L. M. Chatterjee of the Physics Department for help in making the spectrographs.

VARIATIONS IN THE ELECTROCHEMICAL PROPERTIES OF SILICIC ACID AND HYDROGEN BENTONITE SOLS WITH TEMPERATURE.

BY JNANENDRANATH MUKHERJEE, BARADANANDA CHATTERJEE
AND AMITABHA SEN.

Variation with temperature of free and total acidity, degree of dissociation and forms of the titration curves of silicic acid sol and hydrogen bentonite sol are given

Investigations on the electrochemical properties of colloidal acids carried out in this laboratory (J. N. Mukherjee, *et al*, *Indian J Agric. Sci.*, 1932, **2**, 638; 1934, **4**, 733; 1936, **6**, 517; *Trans. Nat. Inst. Sci. India*, 1937, **1**, 227; J. N. Mukherjee, *Kolloid Z.*, 1933, **82**, 257; 1933, **65**, 72; 1934, **67**, 178; Mitra, *Indian J. Agric. Sci.*, 1936, **6**, 555, 1940, **10**, 317; Mitra, Mukherjee and Bagchi, *ibid.*, 1940; **10**, 303, Chatterjee, *J. Indian Chem. Soc.*, 1939, **16**, 589; 1939, **16**, 609) show that silicic acid, hydrogen clay and hydrogen bentonite sols have measurable free and total acids. The titration curves of the sols with bases show definite inflexion points. The p_H at inflexion depends on the nature of the base used and also on the nature of the salt when titrated in presence of the latter. The titration curves of silicic acid sols with dilute solutions (0.01N) of NaOH, Ba(OH)₂ and Ca(OH)₂ show inflexion points in the acid region between p_H 4.6 and 5.6. The total acid neutralised at the inflexion points is the same for all these bases. The p_H at inflexion, however, increases in the order NaOH > Ba(OH)₂ > Ca(OH)₂. In the case of hydrogen clay and hydrogen bentonite sols, the amount of acid neutralised by different bases at the inflexion points are in the order Ca(OH)₂ > Ba(OH)₂ > NaOH. The degree of dissociation, determined by the ratio of free to total acids, has values between 0.5 and 1.0 in the case of silicic acid sols and usually between 0.5 and 1.0 with hydrogen clay and hydrogen bentonite sols. Variations with temperature of the free and total acids, degree of dissociation and the forms of the titration curves of silicic acid sols and one hydrogen bentonite sol are given in this paper.

The free and total acids (Table I) of silicic acid and hydrogen bentonite sols do not materially change with temperature between 1° and 50°.

TABLE I.

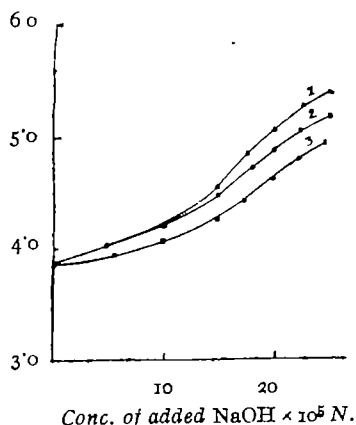
System	p_H			Free acidity $\times 10^5 N.$			Total acidity $\times 10^5 N.$			Degree of dissociation.		
	1°	35°	50°	1°	35°	50°	1°	35°	50°	1°	35°	50°
Silicic acid sol U (18 g./litre)	4'34 4'38	4'37 4'38	4'41	4'3	4'2	4'0	4'0(4'70)*	4'2(4'75)	4'9(4'75)	completely dissociated		
Silicic acid sol W (15'6 g./litre)	3'86 3'86	3'86 3'85	3'85	13'8	13'8	14'1	17'4(5'0)	17'8(4'85)	18'2(4'65)	0'79	0'77	0'77
Hydrogen bentonite sol (11 g./litre) $SiO_2 R_2 O_3 = 2'83$	3'95 3'97	4'06	4'03	10'96	8'7	9'3	275(8'5)	282'5(7'8)	285(7'75)	0'39	0'31	0'33

* Figures within brackets give p_H at inflexion.

A fixed amount of acid is thus neutralised at the inflexion point and the inflexion point possesses a special significance in this sense.

FIG. 1.

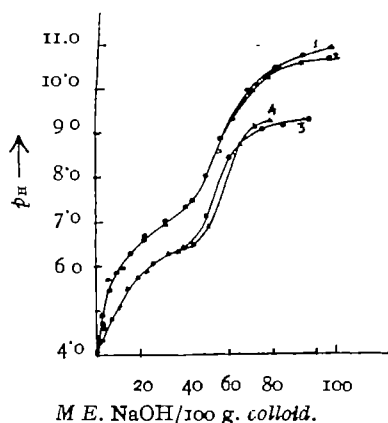
Silicic acid sol W.



Curves 1—3 refer to titration at 1°, 35° and 50° respectively.

FIG. 2.

Hydrogen bentonite sol.



Curves 1 & 2 refer to titration at 1°.

Curves 3 & 4 refer to 35° and 50° respectively.

The potentiometric titration curves of silicic acid sol U with NaOH at different temperatures practically coincide with one another. Those of sol W (Fig. 1), though giving almost the same total acidity at the inflexion

points show a stronger buffering as the temperature is increased. The titration curves (Fig. 2) of the hydrogen bentonite sol at 35° and 50° are almost coincident but that at 1° shows a smaller buffering.

Unlike acids in true solution, the degree of dissociation of silicic acid and hydrogen bentonite sols do not materially change between 1° and 50°. This observation is of considerable theoretical importance and will be discussed in a fuller paper. The effect of temperature on the free and total acids as also on the degree of dissociation appears to be capable of explanation on the basis of the theory of double layer and secondary adsorption of ions (Mukherjee, *Phil. Mag.*, 1922; **44**, 321; *Trans. Faraday Soc.*, 1921, **16**, 103; .

The authors take this opportunity to express their sincere thanks to the Imperial Council of Agricultural Research, India under which body one of the authors (B. Chatterjee) is employed.

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Received March 5, 1941.

REVIEWS

An Introduction to the Kinetic Theory of Gases. BY SIR JAMES JEANS. PUBLISHED BY THE CAMBRIDGE UNIVERSITY PRESS, 1940. PP. 311. PRICE 15 SH. NET.

We welcome with great pleasure this new book by Sir James Jeans on the Kinetic Theory of Gases. The author's classical book "The Dynamical Theory of Gases" which is the first treatise on the subject presented in English has been the source of inspiration to the physicists and mathematicians alike since its publication in 1904. In the subsequent editions of this classical book the treatment of Quantum Theory was also incorporated. But in spite of its comprehensiveness the book proved to be inconvenient to the physicists in general on account of the stiffness of mathematical treatment. The present book will prove to be more inviting to students of science because of its lucidity and less forbidding nature and being less costly it is within the reach of average students.

The special feature of the present work is that the book has been presented from the view point of physicists' need for clearness and directness of treatment rather than mathematicians' need for rigorous proof. It covers almost the same ground of his earlier book but in a more lucid and physical manner, and all that is of physical interest in his earlier treatise has been retained. Matters of purely mathematical interest have in general been discarded. The book will thus prove to be very helpful to the students of physics and physical chemistry and will also provide equipment necessary for undertaking an advanced study on the subject.

Although less imposing in appearance than the author's former book, some new materials have been included, such as experimental tests of Maxwell's law of distribution of velocities, Perrin's researches on Brownian movement, etc. But it should also be pointed out that many interesting subjects of recent development have been omitted. We would have certainly been very glad to see the subjects of Aerostatics, Fluctuation, Electric and Magnetic properties of Gases and Low Pressure incorporated in this book in the author's inimitable way of writing. We have thus been deprived of his masterly treatment of these newer phases of the subject, which would prove to be of great advantage to advanced students of science. But we must rest content that there must have been strong

reasons in the opinion of this Master Mind for not incorporating them in this small edition. But may we not expect to hear of these subjects from this great teacher of Kinetic Theory in a future edition or in his future book ?

The publication has a nice get up characteristic of the Cambridge University Press. We must congratulate the publishers on their effort to bring out such an important treatise.

S. N.M.

Spectrochemical Abstracts Vol. II (1938-39). EDITED BY ERNEST H. S. VAN JOMEREN. PUBLISHED BY ADAM HILGER LIMITED, 98, ST. PANCRA'S WAY, LONDON, N. W. 1.

This small book of 38 pages contains an up-to-date biography and reference to the literature on the application of spectroscopic methods to chemical problems. The book is divided into two parts. The first part contains references arranged alphabetically under the author's names. The second part gives the abstracts proper divided into different sections in which important spectrochemical work has been carried out including sections on Methods and Accuracy, Theory and Principles, General papers and Reviews, Charts and Tables, Books etc. Published in February 1941 the book supplies an up-to-date information on the literature and will prove very useful to every one interested in spectrochemical work.

S. N. M.

Practical Applications of Recent Lac Research.—EDITED BY H. K. SEN AND PUBLISHED BY THE INDIAN LAC RESEARCH INSTITUTE. PP. 84 + X.

A useful handbook of 84 pages containing most of the important informations about lac and its application to modern industries. The first twelve chapters describe the different kinds of commercial lac, and the various industries in which it is, or can be profitably consumed. These are followed by one on lac-cultivation, which is also full of interest. Then comes a series of appendices concerning standard specifications and tests of lac at different stages, and short notes on the manufacture of urea, formaldehyde, melamine and calcium stearate. Finally, the book ends in a comprehensive bibliography of the more important work done on subjects connected with lac, both in the Institute as well as abroad. The book is copiously illustrated with diagrams and plates ; these together with the cost-sheets that come in every section, afford a substantial insight into the industry. The chapter on shellac plastics is quite useful in indicating the role this indigenous material is capable of playing in this important industry of the time. The get-up of

the book is excellent; no price has been mentioned, but considering the usefulness of the book, any reasonable price would be quite justifiable.

C.B.

Methane. Its Production and Utilisation. BY J. P. LAWRIE. PUBLISHED BY CHAPMAN AND HALL, LTD. PP. 66 + VII. PRICE 6 SH.

This brochure of 63 pages is well got up and contains useful statistical data regarding methane and the probable quantities in which it could be produced by the utilisation of coke-oven gases, coal and coal gas, water gas, and sewage. The chapter on compression is useful. In his attempts to establish the value of compressed methane as an automobile fuel, the author has made certain assumptions, which, although establishing its importance as an emergency fuel, hardly justifies its use as a petrol substitute in normal times. On the other hand, he appears to have entirely overlooked the subject of chemical utilisation of the hydrocarbon, *e.g.*, its conversion into formaldehyde, methyl alcohol, etc. There exists quite a considerable bulk of work on this subject of which no reference is given, excepting a bare mention that methane can be oxidised by means of catalysts or ozonised oxygen into methyl alcohol and formaldehyde. On the whole this little book is quite informative, although specialists can hardly draw much information for their use. Moreover, its price of six shillings seems to be too high for general use as a text book.

C.B.





COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS. PART VIII. RESOLUTION OF COBALTIC TRISBIGUANIDE COMPLEX INTO ITS OPTICALLY ACTIVE ENANTIOMERIDES.

BY PRIYADARANJAN RÂY AND NIHAR KUMAR DUTT.

Cobaltic *trisbiguanidinim* chloride has been resolved into its optically active enantiomerides by combining with *d*-tartaric acid and *d*-camphorsulphonic acid. The *diastereoisomerides*, chloro-*d*-tartrate, *d*-tartrate and *d*-camphorsulphonate of the *laevo* and *dextro* cobaltic *trisbiguanide* base, have been prepared in the pure state. The *l*-salt in all cases is less soluble.

A solution of the chloro-*d*-tartrate of the racemoid complex base deposited crystals of only the *laevogyrate* on fractional crystallisation in the cold till the entire solution was dried up. This is possibly the first instance of a complex inorganic salt manifesting the phenomenon of "*asymmetric transformation of the second order*" as described by Kuhn. Further evidence on the point is furnished by the study of the "*addition curve*" obtained by gradually adding the racemoid base to a solution of *dextro*-tartaric acid and observing the rotation after each addition. It has been shown that in a solution of the chloro-*d*-tartrate of the racemoid complex there is an equilibrium between the *dextro* and the *laevo* salt with the former in slight excess. From the slight *dextro*-rotatory mother-liquor after the separation of the first crop of *laevogyrate* from a solution of chloro-*d*-tartrate of the racemoid complex, pure *dextrogyrate* was obtained by repeated fractional precipitation with alcohol. A change in the external condition by changing the nature of the solvent helped to isolate the pure *d*-salt, which could not be obtained from aqueous solution.

A solution of the *d*-tartrate of the racemoid complex, though exhibiting asymmetric transformation, can, however, be normally fractionated giving pure *laevo*- and *dextrogyrates* as the least and the most soluble fractions respectively, due to favourable solubility and stability relationship.

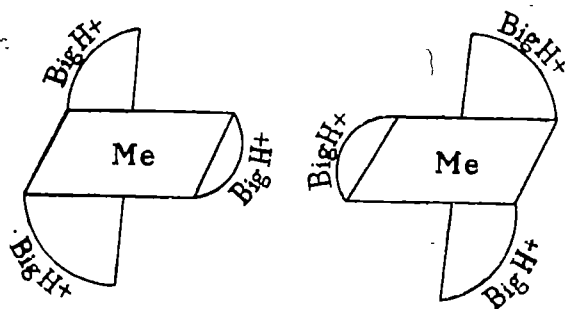
From the pure *laevo*- and *dextrogyrate* of the chloro-*d*-tartrate pure optically active enantiomerides of the sulphate, chloride and nitrate of the complex base were prepared. Their molecular rotations were quite high, suggesting an unsymmetrical co-ordination of the otherwise symmetrical biguanide molecules around the central atom, as was assumed by Rây and Saha in the first paper of the series.

In a previous communication of this series an account of the preparation and properties of cobaltic *trisbiguanidine* and its various salts was given (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, 16, 62). The constitution of biguanide complexes with tervalent metals like chromium and cobalt has also been thoroughly discussed in the first paper of the series (Rây and Saha, *J. Indian Chem. Soc.*, 1937, 14, 670). Biguanide, like ethylenediamine, is a base, and a stronger base too, and it has been shown before (Rây and Saha, *loc. cit.*) that it serves as a "chelate" or bidentate molecule like the latter. It differs, however, from ethylenediamine in certain other respects.

In the first place, unlike ethylenediamine it does not behave as a neutral group or pseudo-base during co-ordination, but, on the other hand, acts as having an *aci*-group in the molecule in spite of its strong basic character. Consequently, it gives rise to the formation of hexa-co-ordinated inner complex salts with tervalent chromium and cobalt. The inner metallic complexes, thus formed, are not non-electrolyte though the primary valencies of the metal ions are fully satisfied. Due to the presence of a free amino-group in each biguanide molecule even after co-ordination, an inner metallic complex salt of the *second order* of a special kind is thereby produced, which makes the co-ordinated chromium or cobalt complex a tervalent cation. Secondly, though like ethylenediamine, its molecule by itself is symmetrically constituted, still it co-ordinates with the metal atom in an unsymmetrical manner (*cf.* Rây and Saha, *loc. cit.*).

Like *tris*ethylenediamine complexes, the *tris*biguanide complexes also possess no plane or centre of symmetry and hence are resolvable into their

Fig. 1.



[Big H = one biguanide molecule.]

optically active antipodes, as represented by the following structures (Fig. 1).

As a matter of fact, the *tris*biguanide complexes will present a somewhat lower order of symmetry than those of *tris*ethylenediamine due to the unsymmetrical co-ordination of the biguanide

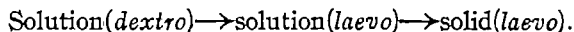
molecule as mentioned above.

An attempt to resolve the chromium *tris*biguanide salts, as stated before (Rây and Dutt, *loc. cit.*), did not succeed well under usual circumstances, when combined with an active acid like *d*-tartaric acid, due to their more or less rapid hydrolysis into *bis*biguanide derivatives. The cobaltic *bis*-biguanide complexes, being on the other hand quite stable, have been successfully split up into their enantiomorphous isomerides; the preparation and properties of the latter, as well as of their *diastereoisomerides* and of the corresponding partial racemates, are described in the present paper.

The resolution was accomplished by combining the complex ion either with *d*-tartaric acid in the form of *d*-tartrate or chloro-*d*-tartrate, or with *d*-camphorsulphonic acid.

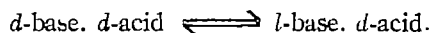
An anomalous observation was, however, made during the fractional crystallisation of the chloro-*d*-tartrate. On allowing a solution of the

chloro-*d*-tartrate of the racemoid complex to crystallise slowly at the room temperature, the first crop of crystals, that separated from the solution, was found to be *laevo*-rotatory with $[\alpha]_D^{25} = -335^\circ$. This retained its rotation unchanged on further fractionation, proving that it is the pure *laevogyrate* of the *diastereoisomerides*. This evidently contradicts Werner's generalisation regarding the comparative solubility of chloro-*d*-tartrates of the optically active antipodes of cobaltic complexes (Werner, *Ber.*, 1912, 45, 865), which assumes that the chloro-*d*-tartrate of the *d*-cobaltic complex always forms the less soluble variety. Observations have also been made by Jaeger showing that Werner's conclusion in this respect is erroneous (cf. Jaeger, "Spatial Arrangement of Atomic Systems and Optical Activity," McGraw Hill Book Co. Inc., 1930, p. 92). There is, therefore, no direct relationship between the configuration of the molecules and their relative or absolute solubility. The mother liquor from the first crop of crystals was found to be *dextro*-rotatory, but when allowed to crystallise deposited successive crops of only the *laevo*-isomeride till the entire solution was practically dried up. There is thus a continuous transformation in solution from the *dextro*- to the less soluble *laevo*-variety as represented below:



Both the *diastereoisomerides* were formed in equal amounts in solution to begin with and tend to approach an equilibrium as they are mutually interconvertible; but before the kinetic equilibrium is established, the less soluble *laevo*-salt separates out from the solution. This ultimately leads to a complete conversion of the *dextro*- into the *laevo*-salt. An explanation of the anomaly can thus be offered.

Similar phenomenon was already observed in the case of many organic compounds and was named by Kuhn (*Ber.*, 1932, 65, 49) as "*asymmetric transformation of the second order*." According to Kuhn a "*first order transformation*" is one in which neither of the two interconvertible *diastereoisomerides* separates out from the solution but may exist in the latter in different proportions:

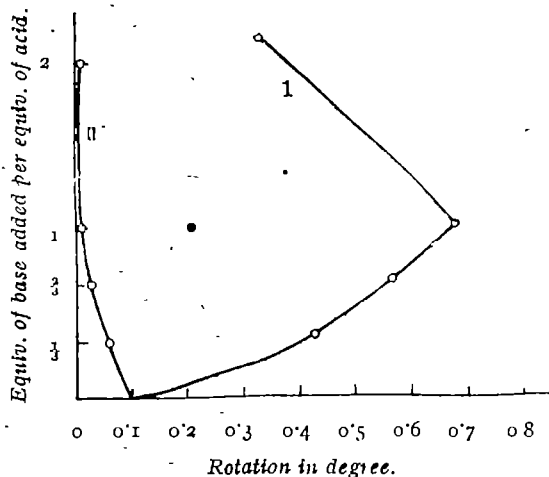


Jamison and Turner (*J. Chem. Soc.*, 1938, 1646) have recently shown that a study of the "addition curve," as named by them, which expresses the rotation as a function of the acid: base ratio, serves as a reliable means of investigating the phenomenon of asymmetric transformation.

In the present case as well, it was noticed that by the gradual addition of the racemic base to a solution of the *d*-tartaric acid the rotation of the latter abnormally increased till an equivalent amount was added, after which

the further addition of the base decreased the rotation. The addition curve, thus obtained, is shown in Fig. 2.

Fig. 2.



The form of the addition curve I (Fig. 2) furnishes a distinct evidence of the asymmetric transformation occurring in the solution of cobaltic bisbiguanide-*d*-tartrate.

Curve II (Fig. 2), obtained by the gradual addition of cobaltic hexammine carbonate to a solution of *d*-tartaric acid, has also been added to account for the influence of salt formation on the rotation of the acid. This effect is negative here and reduces the rotation. A 0.5% solution of tartaric acid was used in these experiments and this was taken to represent unit equivalent for the acid.

The chloro-*d*-tartrate of the *dextro*-base was, however, obtained in the pure crystalline state from the *dextro*-rotatory mother-liquor after the separation of the first crop of the *laevo*-diastereoisomeride by immediate fractional precipitation with alcohol. This suggests that the equilibrium condition of the system corresponds to an excess of the *dextro*-gyrate and hence the product obtained by immediate precipitation with alcohol, in which both the *diastereoisomerides* are insoluble, contains an excess of the complex *dextro*-salt. The isolation of the pure *dextro*gyrate from this by fractional precipitation with alcohol is indicative of the slow rate of transformation in solution leading to an equilibrium. This has been actually verified by experiments. For the slight *dextro*-rotation of a freshly prepared solution of the chloro-*d*-tartrate of the racemoid has been found to

increase gradually with time to a constant maximum value. This same equilibrium rotation was also arrived at starting from a solution of the chloro-*d*-tartrate of the laevo-rotatory as well as of the dextro-rotatory complex. Thus, approaching from three different directions the same equilibrium rotation $[\alpha]_D^{46.1} = +14^\circ$ was obtained. The concentration of the solution employed was 1% in all cases. The corresponding value at 25° determined from the partial racemate was $[\alpha]_D^{25} = +31^\circ$. The initial specific rotation of a freshly prepared solution of the partial racemate was found to be $[\alpha]_D = +6^\circ$ only, the temperature effect on its rotation is practically negligible and lies within the limits of experimental errors. $[\alpha]_D^{46.1}$ for the pure *dextro*-diastereoisomeride is equal to 340° . The equilibrium composition calculated from the above values is 51.2% *d*-salt and 48.8% *l*-salt at 46.1° and the equilibrium constant K at the same temperature is equal to 1.049. Similarly the equilibrium composition at 25° is 53.75% *d*-salt and 46.25% *l*-salt, and $K_{25} = 1.1622$. From the values of K at the two temperatures, the heat evolved in the transformation is calculated according to van't Hoff's equation. This gives a value of 923 calories. The transformation process (*l*-salt \rightarrow *d*-salt) is, therefore, an exothermic one and K decreases with temperature. The free energy decrease of the system in this transformation, ΔF , is thus 30.4 calories at 46.1° and 89.1 calories at 25° . In conformity with the greater stability of the *dextro*-salt, a solution of the latter requires about 9 days to reach the equilibrium rotation value at 46.1° , for which the *laevo*-salt requires about 7 days.

The pure diastereoisomerides are quite stable but lose their water and become anhydrous at 62° without any change in their optical activity. The activity remains unchanged even when they are heated to 105° . The partial racemate, like the active isomerides also becomes anhydrous at 62° .

No anomaly was, however, observed when the complex racemate was split up by means of *d*-tartaric acid in the form of pure tartrate or by *d*-camphorsulphonic acid. The two diastereoisomerides separated normally in these cases during fractional crystallisation—here also the laevogyrate being less soluble, separated out first. That the *dextro*- and the *laevo*-salt can thus be obtained in the pure state in spite of their interconvertibility leading to an equilibrium indicates a more favourable solubility and stability relationship (i.e. a comparatively less difference in solubility and a slower transformation rate).

From the two diastereoisomerides, thus prepared, the pure optically active enantiomorphous isomerides of the chloride, sulphate and nitrate of the complex base were obtained with specific and molecular rotations of $[\alpha]_D^{31} = \pm 450^\circ$, $\pm 362.5^\circ$, $\pm 388^\circ$, and $[M]_D^{31} = \pm 2105^\circ$, $\pm 2062^\circ$, and

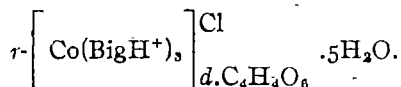
$\pm 2125^\circ$ respectively. The corresponding values for the chloride and nitrate of the complex cobalt *tris*ethylenediamine base are $[M]_D = \pm 608^\circ$ and $\pm 562^\circ$ only. A higher rotation for the complex cobaltic *tris*biguanidinium ion, compared to that of *tris*ethylenediamine cobaltic ion, is indicative of a lower degree of symmetry for the former. This furnishes an indirect evidence in support of the constitution of *tris*biguanide complexes (an unsymmetrical co-ordination of the symmetrical biguanide molecules) as suggested by Rây and Saha (*loc. cit.*).

The optically active antipodes of the cobaltic *tris*biguanide ion in all cases (chloride, sulphate and nitrate) are quite stable in the solid state and retain their rotation unchanged even up to a temperature of 105° . In aqueous solution they can be maintained without any change up to a temperature of 35° for over 12 hours. At about 40° they show slow racemisation in solution, which becomes almost instantaneous at the boiling temperature. Dilute solutions of alkalis also bring about rapid racemisation, acids in somewhat larger concentration react in the same way.

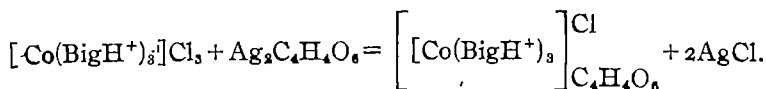
A detailed study of the kinetics of interconversion of the active *diastereoisomerides*, the velocity of racemisation of the pure active *enantiomerides* and the catalytic effect of many simple and complex ions upon it, as well as the nature of the change associated with the phenomenon of racemisation will form the subject of a separate communication.

EXPERIMENTAL.

Racemic Cobaltic trisBiguanidinium Chloro-d-tartrate:



This was prepared by the double decomposition of the complex cobaltic *tris*biguanidinium chloride (Rây and Dutt, *loc. cit.*) with one molecule of silver *d*-tartrate. The solution, filtered from the silver chloride, was evaporated to dryness on the water-bath. The crystals were kept in air, till their weight became constant.



The substance forms orange-yellow, silky, rectangular plates, moderately soluble in water. When heated to 62° , the crystals lose their water and

become anhydrous. (Found : Cl, 5.45 ; Co, 9.30. Calc. : Cl, 5.50 ; Co, 9.28 per cent).

l-Cobaltic trisBiguanidinium Chloro-d-tartrate.—The laevogyrate was obtained in the form of orange-coloured, silky, thin rectangular plates by the fractional crystallisation of the above described partial racemate. The crop of crystals, that separated at the laboratory temperature, formed the pure *laevo*-salt. From a cold saturated solution of the racemate, the first crop separated on keeping only for a few hours. The crystals were filtered, washed first with cold water, then with alcohol and finally dried in air. (Found : Cl, 5.45 ; Co, 9.41. Calc. : Cl, 5.50 ; Co, 9.28 per cent).

It possesses the same composition as the partial racemate and loses all its water when heated to 62° without any change in its activity.

$$[\alpha]_D^{21} = -335^\circ. \quad [M]_D^{31} = -2129^\circ.$$

It retains its activity unchanged even when heated to 105° for hours.

d-Cobaltic trisBiguanidinium Chloro-d-tartrate.—The mother-liquor from the above described *laevo*-salt was at once subjected to fractional precipitation by means of alcohol. After removing several crops of crystals, till there was no further appreciable increase in the dextro-rotation of the separated solid, the residual liquor was completely precipitated with alcohol. The final precipitate was redissolved in cold water and again fractionally precipitated with alcohol. The process was repeated with the most soluble fraction in each case until the rotation of the finally separated product became maximum and constant.

It forms orange-coloured, irregular thick plates, highly soluble in water. (Found : Cl, 5.51 ; Co, 9.40. Calc. : Cl, 5.50 ; Co, 9.28 per cent).

It possesses the same composition as the *l*-salt and like the latter becomes anhydrous at 62°.

$$[\alpha]_D^{21} = +340^\circ. \quad [M]_D^{31} = +2161^\circ.$$

In all other respects it resembles the *laevo*-salt.

d-Cobaltic trisBiguanidinium Sulphate $d\text{-}[\text{Co}(\text{BigH}^+)_3]_2(\text{SO}_4)_3, 7\text{H}_2\text{O}$.

The complex *dextro*-sulphate was obtained as sparingly soluble, orange-coloured, prismatic needles from the chloro-*d*-tartrate of the *dextro* complex by precipitation with a cold saturated solution of ammonium sulphate. The crystals were washed first with ice-cold water, then with alcohol and afterwards dried in air. (Found : S, 8.42 ; Co, 10.41. Calc. : S, 8.44 ; Co, 10.37 per cent). $[\alpha]_D^{21} = +362.5^\circ$. $[M]_D^{31} = +4125^\circ$.

l-Cobaltic trisBiguanidinium Sulphate.—The *laevo*-sulphate was obtained in a similar manner like its *dextro*-isomeride from the chloro-*d*-tartrate of the *laevo*-complex. It possesses the similar composition and properties as its *dextro*-analogue. (Found : S, 8'42 ; Co, 10'35. Calc.: S, 8'44 ; Co, 10'37 per cent). $[\alpha]_D^{31} = -362.5^\circ$. $[M]_D^{31} = -4125^\circ$.

d-Cobaltic trisBiguanidinium Chloride : *d*-[Co(BigH⁺)₃]Cl₃.—For its preparation the above described *d*-sulphate was digested in the cold with a saturated solution of the calculated quantity of barium chloride. The filtrate from barium sulphate was then evaporated to dryness in *vacuo*. The *dextro*-chloride forms readily soluble, orange-coloured crystals, appearing as rectangular prisms under the microscope. (Found : Co, 12'63. Calc. : Co, 12'59 per cent). $[\alpha]_D^{31} = +450^\circ$. $[M]_D^{31} = +2108^\circ$.

l-Cobaltic trisBiguanidinium Chloride.—The *l*-chloride was obtained like its *d*-isomeride from the *l*-sulphate and barium chloride. It forms orange-coloured, prismatic crystals, very soluble in water and has the same composition as its *d*-analogue. (Found : Co, 12'62. Calc. : Co, 12'59 per cent). $[\alpha]_D = -449^\circ$. $[M]_D^{31} = -2103^\circ$.

It can be heated to 105° without any change in its activity.

d-Cobaltic trisBiguanidinium Nitrate : *d*-[Co(BigH⁺)₃](NO₃)₃.—This was obtained like the previous compounds from the *d*-sulphate and barium nitrate. It forms orange-coloured prisms, soluble in water. Found : Co, 10'95. Calc. : Co, 10'77 per cent). $[\alpha]_D^{31} = +388^\circ$. $[M]_D^{31} = +2126^\circ$.

l-Cobaltic trisbiguanidinium nitrate was prepared like its *d*-isomeride from the *l*-sulphate and barium nitrate. It forms moderately soluble, reddish yellow, irregular prisms and has the same composition as its *d*-analogue. (Found : Co, 10'90. Calc. : Co, 10'77 per cent).

l-Cobaltic trisBiguanidinium *d*-Camphorsulphonate : *l*-[Co(BigH⁺)₃]*d*-(C₁₀H₁₃OSO₃)₃.—This was obtained by the fractional crystallisation in the cold of the corresponding partial racemate previously described (Rây and Dutt, *loc. cit.*). The first crop of crystals obtained was further fractionated, always using the least soluble fraction, till two such fractions of two consecutive operations showed identical maximum rotation. The substance forms flesh-coloured crystals, moderately soluble in water. They were washed first with ice-cold water and then with alcohol. The crystals were dried in vacuum over concentrated H₂SO₄. (Found : Co, 5'71. Calc.: Co, 5'61 per cent). $[\alpha]_D^{31} = -202$. $[M]_D^{31} = -2131^\circ$.

d-Cobaltic trisbiguanidinium *d*-camphorsulphonate was prepared by the fractional crystallisation in the cold of the mother-liquor remaining after the separation of the first crop of crystals from a saturated

aqueous solution of the corresponding partial racemate. After several successive fractions were rejected, the solution finally deposited a strongly dextro-rotatory solid. This was purified by repeated crystallisation. It possesses the same composition as its *l*-analogue. (Found : Co, 5.70. Calc. : Co, 5.61 per cent). $[\alpha]_D^{31} = +202^\circ$. $[M]_D^{31} = +2131^\circ$.

Racemic cobaltic trisbiguanidinium d-tartrate, $r\text{-}[\text{Co}(\text{BigH}^+)_3]_2 \cdot \text{d}(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5\text{H}_2\text{O}$ was obtained by digesting the solid base in the cold with a saturated solution of *d*-tartaric acid. The orange-coloured crystals of the tartrate were filtered, washed first with cold water and then with alcohol. They were afterwards dried in air. (Found : C, 22.81; H, 5.21; Co, 9.41. Calc. : C, 22.89; H, 5.09; Co, 9.38 per cent).

l-Cobaltic trisbiguanidinium d-Tartrate.—*Dextro*-tartrate of the *laevo*-complex was obtained by the fractional crystallisation of a saturated solution of the above described partial racemate. The first crop of crystals obtained was subjected to further fractionation, always employing the least soluble fraction for the purpose, till two consecutive fractions gave a maximum identical rotation. It resembles the partial racemate in properties and possesses the same composition. (Found : C, 22.75; H, 5.15; Co, 9.40. Calc. : C, 22.89; H, 5.09; Co, 9.38 per cent). $[\alpha]_D^{31} = -330^\circ$. $[M]_D^{31} = -4151^\circ$.

d-Cobaltic trisbiguanidinium d-tartrate was prepared by fractional crystallisation from the mother-liquor remaining after the separation of the first crop of crystals in the preparation of the *l*-salt from a solution of the partial racemate as described above. After several successive fractions were rejected, the solution finally deposited a strongly dextro-rotatory solid. This was then purified by repeated crystallisation. It possesses the same composition as its *l*-analogue. $[\alpha]_D^{31} = +332$. $[M]_D^{31} = +4176^\circ$.

All measurements were made in a Fianz Schmidt and Haensch's polarimeter with a trisected field of vision and provided with an electrical heating arrangement by which the temperature could be maintained constant to $\pm 0.1^\circ$.

Our best thanks are due to Prof. J. N. Mukherjee, D.Sc. for providing facilities of making the polarimetric measurements in his laboratory.

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Received March 1, 1941.

COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS. PART IX. ACTION OF MERCURIC CHLORIDE AND SILVER NITRATE UPON CHROMIUM AND COBALTIC TRISBIGUANIDINIUM HYDROXIDES AND THE CONSTITUTION OF BIGUANIDE METAL COMPLEXES.

BY PRIVADARANJAN RÂY AND SUSHTIL KUMAR SIDDHANTA.

According to the constitution suggested for the biguanide metal complexes in a previous communication of the series it was expected that the complex metal biguanide bases should behave like ammonia or the amines. An additional evidence in this respect has been brought forward in this paper by a study of the behaviour of these complex bases towards mercuric chloride and silver nitrate. By adding mercuric chloride to chromium and cobaltic trisbiguanide bases, the compounds $\text{Cr}(\text{Big} \cdot \text{HgCl})_3$ and $\text{Co}(\text{Big} \cdot \text{HgCl})_3 \cdot \text{HgCl}_2$, were obtained, which closely resemble the infusible white precipitate in their constitution and properties. It has also been shown that with AgNO_3 the cobaltic trisbiguanide hydroxide forms the compound, $\text{Co}(\text{BigH} \cdot \text{AgOH})_3$, aq., resembling silver ammine hydroxide.

Two more compounds of mercuric chloride with biguanide and ethylenediamine hydroxide, $\text{ClHg} \cdot \text{NH} \cdot \underset{\text{NH}}{\underset{\parallel}{\text{C}}} \cdot \text{NH} \cdot \underset{\text{NH}}{\underset{\parallel}{\text{C}}} \cdot \text{NH} \cdot \text{HgCl}$ and $2 \left[\begin{array}{c} \text{CH}_2 \cdot \text{NH} \cdot \text{HgCl} \\ | \\ \text{CH}_2 \cdot \text{NH} \cdot \text{HgCl} \end{array} \right] \cdot \text{HgCl}_2 \cdot 7\text{H}_2\text{O}$ respec-

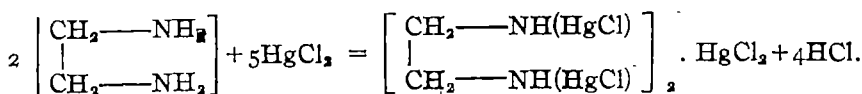
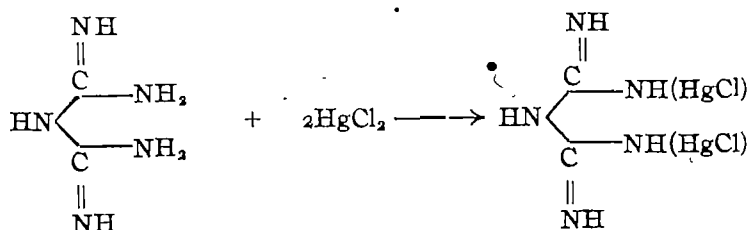
tively, also of the infusible white precipitate type, have been described

Besides, double salts of the composition, $[\text{Cr}(\text{BigH}_2)_3]\text{Cl}_3 \cdot 3\text{HgCl}_2$; $[\text{Co}(\text{BigH}_2)_3]\text{Cl}_3 \cdot 3\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 5\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ (in two different crystalline forms and colour) have been prepared and their properties studied.

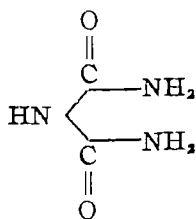
A detailed discussion regarding the constitution of metal biguanide complexes was made in the first paper of the series and a structure based on their chemical and physical properties was also suggested (Rây and Saha, *J. Indian Chem. Soc.*, 1937, **14**, 670). It was shown that three biguanide molecules, functioning as bidentate or double-bonding groups, co-ordinate with each metal atom (Cr^{3+} or Co^{3+}) to form an inner metallic complex with one of the end-amino groups of each biguanide molecule remaining free for further co-ordination or salt formation. This makes the complex as a whole a trivalent cation, representing an inner metallic complex of the second order. The central atoms, Cr or Co, have their primary valencies fully saturated by displacing a hydrogen atom of one of the imino groups ($=\text{NH}$) of each biguanide molecule and cannot, therefore, make any contribution towards the electrical character of the complex ion. Chromium

and cobaltic *trisbiguanidines*, therefore, should behave in aqueous solution to a certain extent like ammonia or the organic amines, and, like the latter, combine with mercuric chloride to form insoluble compounds of the "infusible white precipitate" type. Similarly, with silver nitrate, compounds of the silver ammine type are to be expected. These have actually been verified by experiments as described in this paper.

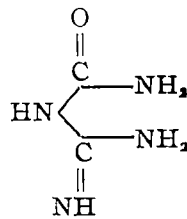
Free biguanide hydroxide or free ethylenediamine hydrate have been found to react with mercuric chloride to give compounds, resembling infusible white precipitate of the following types :



Biguanide is also closely related to biuret and dicyandiamidine :

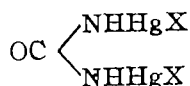


Biuret



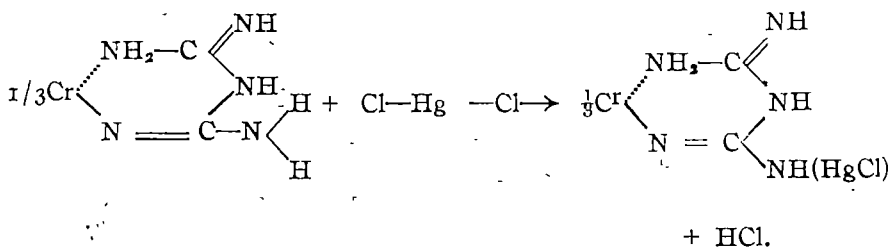
Dicyandiamidine

and it has further been observed that the dicyandiamidine base does not give with mercuric chloride a precipitate of HgO , but a very light yellow insoluble compound of the infusible white precipitate type. Mercuric compounds of biuret of the type $\text{Hg}(\text{C}_2\text{H}_4\text{N}_3\text{O}_2)_2 \cdot 2\text{HgO}$ have already been described by Schiff (*Ber.*, 1896, 29, 299 ; *Annalen*, 1898, 299, 242). Even the pure carbamide like urea, in presence of NaHCO_3 , gives a large number of mercuric derivatives of the infusible white precipitate type which can be represented as



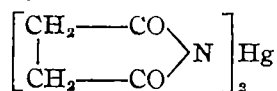
where X may be Cl^- , NO_3^- , OH^- or $1/2 \text{SO}_4^{2-}$ (cf. Ruspaggiari, *Gazzetta*, 1871, 27, 1; Dessaignes, *Annalen*, 1852, 82, 232.)

By treating chromium and cobaltic biguanide bases with mercuric chloride, sparingly soluble compounds of the composition, $\text{Cr}(\text{Big} \cdot \text{HgCl})_3$ and $\text{Co}(\text{Big} \cdot \text{HgCl})_3 \cdot \text{HgCl}_2$ have been prepared ($\text{Big} = \text{C}_2\text{N}_3\text{H}_3$). These resemble strongly the infusible white precipitate in as much as they are very sparingly soluble in water, alcohol or dilute alkalis, but readily soluble in dilute acids, and are slowly decomposed by boiling alkalis. Each biguanide molecule in these compounds takes up evidently one HgCl radical which must displace a hydrogen atom in the free amino group in the otherwise co-ordinated biguanide molecule, according to the scheme given below :



That the hydrogen atoms in the imino groups or the co-ordinated -NH_2 groups are not attacked by HgCl_2 is proved by the fact that on adding HgCl_2 to chromium or cobaltic biguanide chloride (in which the free -NH_2 groups are bound up by salt formation), no substitution compound of the infusible white precipitate type was obtained, but the products form highly crystalline double salts of the type,

$[\text{Cr}(\text{BigH}_2)_3 \cdot \text{Cl}_3] \cdot 3\text{HgCl}_2$ and $[\text{Co}(\text{BigH}_2)_3] \cdot \text{Cl}_3 \cdot 3\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, which are soluble in water and more so in alcohol. Moreover, the displacement of H-atoms in $=\text{NH}$ groups to give compounds of the infusible white precipitate type have not been observed. The mercury compound of succinimide,



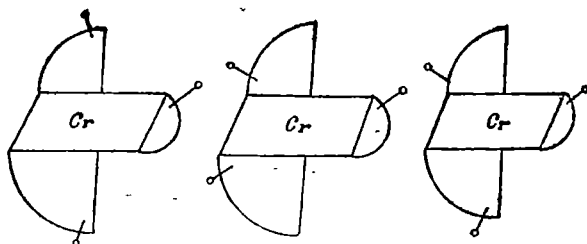
(Dessaignes, *loc. cit.*), is very soluble in water and hence should rather be regarded as a true ionic salt and not a compound of the infusible white precipitate type.

Besides, cobaltic ethylenediamine hydroxide, in which all NH_2 groups are co-ordinated with the central Co atom, cannot give stable compounds of

the infusible white precipitate type. Addition of HgCl_2 to $[\text{Co}(\text{en})_3](\text{OH})_3$ gave a bright yellow precipitate which changed within a few minutes into a brown oxychloride, $2\text{HgO} \cdot \text{HgCl}_2$, even in the cold.

However, a few unstable compounds, somewhat analogous to the infusible white precipitate, have been described by Vortmann and Morgulis (*Ber.*, 1889, 22, 2644). These were obtained by the addition of HgCl_2 solution to that of different cobaltammine chlorides in presence of varying amounts of NaOH . It was assumed by the authors that the substitution of an H-atom of ammonia by HgCl or HgOH radical takes place here even when the ammonia molecule is co-ordinated with the metal atom. It is, however, noteworthy that except in a few cases the analytical results show a considerable deviation from those of the formulae proposed. All these compounds again are unstable and readily break down with dissolution of the complex into a black mass. As the reactions were carried out in solutions rendered strongly alkaline with caustic soda, decomposition of the cobaltammines with liberation of ammonia is not excluded here. It might also happen that the co-ordinated NH_3 molecules exhibit some differences from co-ordinated -NH_2 groups, when reacting with HgCl_2 .

The mercuric chloride derivative of the complex chromium biguanide base was obtained in two different forms: one, the anhydrous, the other as a monohydrate. These differed in their colours. As both the hydrated and the anhydrous varieties were equally stable under ordinary conditions, it seems to suggest a metastable state for the hydrated variety, if, of course, the possibility of space-isomerism due to difference in the position of HgCl groups in the molecule, as shown below, be excluded. The hydrated variety has been found to change into the anhydrous form by prolonged boiling with water.



The dot with the bar (symbol) indicates the position of HgCl group.

Attempts to prepare compounds of the metallic biguanide bases with Nessler's reagent have not been successful. Insoluble brown precipitates

of variable composition were obtained when the complex bases were treated with K_2HgI_4 .

The free metal biguanide base like ammonia may be regarded as an equilibrium mixture of the following :



Mercuric chloride reacts with the anhydrous base $M(\text{BigH})_3$ as with NH_3 .

The silver salts combine with ammonia and organic amines to give, as is well known, the complex silver ammines, where the silver atom occurs generally in twofold co-ordination with ammonia or the amines. Silver compounds of guanidine, biuret and urea, having the compositions $\text{Ag}(\text{CN}_2\text{H}_3)\text{NO}_2$, $\text{Ag}_2(\text{C}_2\text{H}_3\text{N}_3\text{O}_2)$, $\text{Ag}_2(\text{CON}_2\text{H}_2)$ have been described (Hofmann, *Ber.*, 1868, 1, 146; Wisliscenus, Bouné and Goldenberg, *Bei.*, 1874, 7, 287; Mulder, *ibid.*, 1873, 6, 1019). The latter two are regarded as simple salts in which biuret and urea behave as disbasic acids.

By adding silver nitrate to the free biguanide base, no Ag_2O but a white insoluble voluminous precipitate, soluble in ammonia was obtained. This on analysis, however, gave no definite stoichiometric composition.

It was expected that the complex metallic biguanide bases should give with silver oxide compounds analogous to the silver ammine hydroxides. In fact by adding silver nitrate to cobaltic biguanide hydroxide, no silver oxide, but, on the contrary, a pinkish precipitate of the composition, $\text{Co}(\text{BigH}.\text{AgOH})_3.\text{aq}$, was produced (BigH_2 = one biguanide molecule). The compound, however, is not very stable. In this connection it may be mentioned that cobaltamine hydroxide or cobaltic ethylenediamine hydroxide, in which all the NH_2 molecules or $-\text{NH}_2$ groups are co-ordinated to the central cobalt atom and have got no more lone pairs of electrons, gives a precipitate of Ag_2O when treated with AgNO_3 . In fact these complex hydroxides can be prepared in the pure state by treating the corresponding chloride with silver oxide.

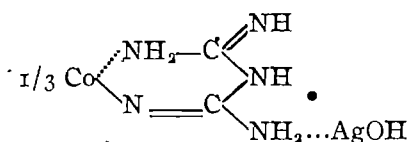
Co-ordination of the silver ion with any of the $=\text{NH}$ groups in the biguanide molecules is highly improbable, since no silver imine complex is known.

Silver succinimide, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CH}_2-\text{CO} \end{array} \rangle \text{NAg}$ (Menschutkin, *Annalen*,

1872, 162, 168), may be regarded as a simple salt of silver, formed by the displacement of the H atom of the $=\text{NH}$ group of the succinimide molecule. All compounds, such as biuret, urea and succinimide, in which one or more hydrogen atoms are replaced by silver to form salt-like compounds, are characterised by having carbonyl ($-\text{CO}-$) groups in the molecule. But no

amidine of the type $\text{R}-\text{C} \begin{smallmatrix} \nearrow \text{NH} \\ \searrow \text{NH}_2 \end{smallmatrix}$ is known to form salt-like compounds with

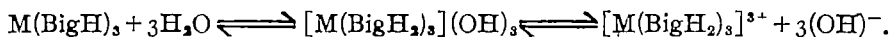
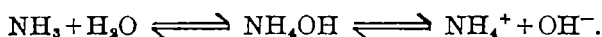
silver; with guanidine, on the other hand, it forms an addition complex, as already stated (Hofmann, *loc. cit.*). The only remaining possibility of the linking of Ag^+ or AgOH with an already co-ordinated biguanide molecule is through the free $-\text{NH}_2$ group, not co-ordinated to the central cobalt atom. The probable structure of the compound under discussion is, therefore, given by :



This is comparable to monamine silver hydroxide ; the large volume of the co-ordinating cobalt-biguanide group probably reduces the co-ordination number of silver, if we assume the hydroxyl group to be ionisable. Alternatively, it may be regarded as a nonionisable compound with co-ordination number of silver equal to 2 as usual.

On adding silver nitrate to chromium biguanide base, no Ag_2O , but a pinkish precipitate having no definite composition was produced. This may be due to the partial hydrolysis of chromium *tris*biguanide base in aqueous solutions into chromium hydroxo-aquo-*bis*biguanide base and free biguanide (Rây and Saha, *loc. cit.*).

The formation of the above described mercury and silver derivatives of cobalt and chromium *tris*biguanide bases furnishes additional evidence in support of the constitution of the biguanide metal complexes suggested by Rây and his co-workers (*loc. cit.*), showing that free metal biguanide bases behave like ammonium hydroxide in aqueous solution :



where $\text{M} = \text{Cr}^{3+}$ or Co^{3+} .

EXPERIMENTAL.

Chromium trisBiguanide Mercuri-chloride.—A solution of freshly prepared and recrystallised chromium *tris*biguanide monohydrate was warmed on the water-bath and an excess of a solution of HgCl_2 in a large volume of water was added to it, drop by drop, with constant stirring ; the

resulting light violet precipitate was filtered and washed first with cold water and then with alcohol. The substance was dried over concentrated H_2SO_4 for 12 hours and then kept exposed to air until it attained a constant weight. [Found: N, 19.51; Cl, 10.09; Cr, 4.83; Hg, 56.46. $\text{Cr}(\text{Big.HgCl})_3$ requires N, 19.87; Cl, 10.07; Cr, 4.92; Hg, 56.94 per cent].

The substance is insoluble in water or solutions of alkali (dil. or conc.), but soluble in dilute mineral acids. On prolonged boiling with strong alkali solutions it suffers slow decomposition.

A rose-red monohydrated derivative of the above compound was obtained when the precipitation was carried out in ice-cold solution. [Found: Cl, 9.84; Cr, 4.67; Hg, 55.88. $\text{Cr}(\text{Big.HgCl})_3 \cdot \text{H}_2\text{O}$ requires Cl, 9.89; Cr, 4.83; Hg, 55.98 per cent].

Double Compound of Cobaltic trisBiguanide Mercuri-chloride with Mercuric Chloride.—A solution of freshly recrystallised cobaltic biguanide hydrate (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, **16**, 621) was heated on a water-bath and an excess of a solution of HgCl_2 in a large volume of water was added to it, drop by drop, with constant stirring. A dull red precipitate appeared; it was filtered hot and washed with water. The product was dried over sulphuric acid in vacuum and then kept exposed to air until it attained a constant weight. [Found: N, 15.70; Cl, 13.23; Co, 4.48; Hg, 60.17. $\text{Co}(\text{Big.HgCl})_3 \cdot \text{HgCl}_2$ requires N, 15.72; Cl, 13.24; Co, 4.41; Hg, 60.08 per cent].

The substance is insoluble in water and alkalis, slightly soluble in alcohol but dissolves readily in mineral acids.

Biguanide Mercuric Chloride.—A solution of biguanide hydroxide, prepared from biguanide sulphate and barium hydrate, was cooled and treated with an excess of cold HgCl_2 solution, and added drop by drop with vigorous stirring, when a flocculent precipitate appeared. This was washed with cold water and dried over concentrated H_2SO_4 in vacuum and afterwards exposed to air till its weight became constant. [Found: N, 12.26; Cl, 12.37; Hg, 69.71. $(\text{ClHg})\text{—NH—C—NH—C—NH(HgCl)}$



requires N, 12.27; Cl, 12.41; Hg, 70.25 per cent].

The substance is insoluble in water, alcohol or alkaline solutions, but soluble in mineral acids.

Compound of Ethylenediamine with Mercuric Chloride.—Several compounds of ethylenediamine with mercuric salts have been described by Scherring ("Chemische Fabrik auf Aktein," Berlin, 1901). He prepared a compound from mercuric chloride and ethylenediamine (m.p. 180°) in the form of white needles, insoluble in water or alcohol, but soluble in

excess of ethylenediamine. Detailed studies as to its formula and constitution do not, however, appear to have been made. It has been observed by us that by adding mercuric chloride solution to ethylenediamine in different proportions or *vice versa* under different conditions, mixtures of various compositions were obtained. A pure compound can, however, be prepared by the following process.

A very dilute solution of ethylenediamine was added, drop by drop, to large excess of a concentrated solution of mercuric chloride with vigorous stirring at the room temperature. A voluminous white precipitate was formed. This was washed with cold water several times, dried in vacuum over sulphuric acid for twelve hours and then exposed to air till it attained a constant weight. {Found : N, 3.84; Cl, 14.63; Hg, 68.96.

$$2 \left[\begin{array}{c} \text{CH}_2\text{NH.HgCl} \\ | \\ \text{CH}_2\text{NH.HgCl} \end{array} \right] \text{HgCl}_2, 7\text{H}_2\text{O}$$
 requires N, 3.84; Cl, 14.58; Hg, 68.8 per cent}.

The substance is slightly soluble in hot water and the solution deposits mercury on a piece of clean strip of copper dipped into it.

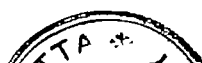
Double Compound of Chromium trisBiguanide Chloride with Mercuric Chloride.—To an ice-cold solution of chromium trisbiguanide hydrochloride (Rây and Saha, *loc. cit.*) a cold solution of mercuric chloride in excess was added, drop by drop, with stirring. The solution, on keeping in the cold, gave a crop of beautiful orange red crystals. These were washed with cold water and dried in air. {Found : Cl, 25.03; Cr, 4.04; Hg, 47.07. $[\text{Cr}(\text{BigH}_2)_3]\text{Cl}_3.3\text{HgCl}_2$ requires Cl, 25.0; Cr, 4.08; Hg, 47.17 per cent}.

The substance is soluble in water and alcohol.

Double Compound of Cobaltic trisBiguanide Chloride with Mercuric Chloride.—To an ice-cold solution of cobaltic trisbiguanide hydrochloride (Rây and Dutt, *loc. cit.*) was added a solution of mercuric chloride in excess and the mixture was stirred for a few minutes, when a crop of beautiful brownish yellow crystals appeared. These were washed with cold water and dried in air. {Found : Cl, 24.35; Co, 4.49; Hg, 45.61. $[\text{Co}(\text{BigH}_2)_3]\text{Cl}_3.3\text{HgCl}_2.2\text{H}_2\text{O}$ requires Cl, 24.19; Co, 4.47; Hg, 45.63 per cent}.

The substance is readily soluble in water and more so in alcohol.

Double Compound of Ethylenediamine Cobaltic Chloride and Mercuric Chloride.—A solution of triethylenediamine cobaltic hydroxide, prepared from its chloride and moist silver oxide, was treated with a concentrated solution of mercuric chloride in excess. A yellow precipitate (A) appeared, which on warming changed readily into a brown-red insoluble substance (B). This was washed with hot water and dried over sulphuric acid in



vacuo. The hot filtrate gradually deposited fine, golden yellow plates of a third substance (C), which were washed with ice-cold water and dried in air.

The substance (A) was very unstable and changed even at 0° readily into (B).

[Found (substance B) : Cl, 10.02; Hg, 85.27. $2\text{HgO} \cdot \text{HgCl}_2$ requires Cl, 10.07; Hg, 85.38 per cent].

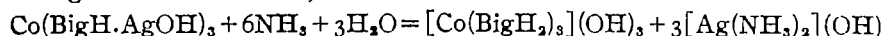
The compound (C) gave on analysis : Cl, 26.68; Hg, 57.86; Co, 3.47. $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 5\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ requires Cl, 26.51; Hg, 57.68; Co, 3.39 per cent. (en = one molecule of ethylenediamine). The compound (C) is readily soluble in water and alcohol.

A compound of the same composition as (C), but of a different colour and crystalline appearance, was prepared by keeping a solution of mercuric chloride mixed with that of trisethylenediamine cobaltic chloride in the cold for sometime. The orange-yellow needles, which separated out, were washed with cold water and dried in air. This substance (D), like (C), was also readily soluble in water and more so in alcohol. It gave on analysis Cl, 26.56; Co, 3.41; Hg, 58.08 per cent. Its crystals appeared as hexagonal orange prisms under the microscope. It can, therefore, be concluded that the double salt $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 5\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ is dimorphous. The orange-yellow variety is the stable form at lower temperature and changes into the golden yellow plates at higher temperature.

Cobaltic Biguanide Silver Hydroxide.—A solution of silver nitrate was added with stirring to an ice-cold solution of cobaltic trisbiguanide hydrate (Rây and Dutt, *loc. cit.*). The resulting precipitate was washed with ice-cold water till free from nitrate. This was dried over H_2SO_4 in *vacuo* for 12 hours. On keeping for a longer period over sulphuric acid the substance partially loses weight and suffers gradual decomposition.

It gave on analysis N, 23.74; Ag, 37.0; Co, 6.52 per cent. Hence $\text{Ag} : \text{Co} : \text{N} = 3 : 1 : 15$. This corresponds to $\text{Co}(\text{BigH} \cdot \text{AgOH})_3$, aq. where $\text{BigH} = \text{C}_2\text{N}_5\text{H}_4$.

The substance forms pink coloured powder and decomposes on boiling in aqueous suspension. It reacts alkaline and readily dissolves in acids. With concentrated ammonia it forms silver ammine hydroxide and cobaltic trisbiguanide base. Thus,



THE TERNARY SYSTEM. AMMONIUM NITRATE-AMMONIUM SULPHATE-WATER AT 25°.

BY R. K. BAHL AND SURJIT SINGH.

In the system NH_4NO_3 -(NH_4)₂ SO_4 - H_2O studied at 25°, two double salts (NH_4)₃ SO_4 , 2 NH_4NO_3 and (NH_4)₂ SO_4 , 3 NH_4NO_3 are formed respectively. No salt hydrate is formed.

The system NH_4NO_3 -(NH_4)₂ SO_4 - H_2O was studied by Massink (*Z. physikal. Chem.*, 1917, **92**, 351). It has been reinvestigated at 25° as a part of the work entailed in the study of the quaternary system, H_2O - K_2SO_4 - KNO_3 -(NH_4)₂ SO_4 - NH_4NO_3 at 25°, still under investigation. The vapour phase has been assumed to be absent and the whole subject has been treated as a condensed system at atmospheric pressure.

The method adopted for the study of the various complexes of ammonium nitrate and ammonium sulphate stirred up to equilibrium at 25° was the same as in the ternary system, potassium nitrate-ammonium nitrate-water at 25° (Bahl and Singh, *J. Indian Chem. Soc.*, 1940, **17**, 441).

The ammonium was determined by the usual distillation method and the nitrate was estimated by Lunge's nitrometer as given by Scott ("Standard Methods of Chemical Analysis", 1925, Vol. I, p. 353). The amounts of sulphate and water were calculated by difference. These values were also checked by estimating sulphate as barium sulphate.

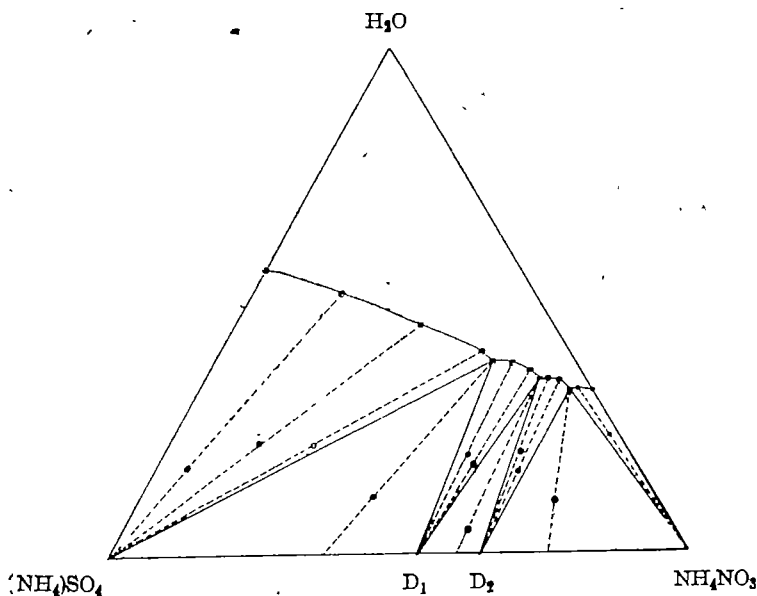


Fig. 1.

The system at 25° is complicated by the existence of two double salts, the compositions of which have been found to be $(\text{NH}_4)_2\text{SO}_4, 3\text{NH}_4\text{NO}_3$ and $(\text{NH}_4)_2\text{SO}_4, 2\text{NH}_4\text{NO}_3$ respectively. It is shown in Fig. 1 and the data for composition by weight for this system at the above temperature are given below.

Solution.		Rest		
NH_4NO_3 .	$(\text{NH}_4)_2\text{SO}_4$.	NH_4NO_3	$(\text{NH}_4)_2\text{SO}_4$.	Solid phases.
68.17%	0 %	NH_4NO_3
65.43	2.25	75.50	1.88	NH_4NO_3
64.10	3.95	72.10	17.62	NH_4NO_3 D_7
61.50	4.56	63.10	20.95	NH_4NO_3 D_2
59.54	6.24	61.91	18.75	D_2
57.62	7.51	60.01	35.61	D_2 D_1
55.78	8.46	54.88	27.43	D_1
51.41	10.83	53.00	27.72	D_1
47.95	13.58	40.51	48.11	D_1 $(\text{NH}_4)_2\text{SO}_4$
45.47	14.92	25.10	53.23	$(\text{NH}_4)_2\text{SO}_4$
32.14	22.21	15.47	62.51	$(\text{NH}_4)_2\text{SO}_4$
15.21	32.97	5.26	77.12	$(\text{NH}_4)_2\text{SO}_4$
...	43.43	$(\text{NH}_4)_2\text{SO}_4$

$D_1 = (\text{NH}_4)_2\text{SO}_4, 2\text{NH}_4\text{NO}_3$. $D_2 = (\text{NH}_4)_2\text{SO}_4, 3\text{NH}_4\text{NO}_3$

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Received March 27, 1941.

THE ACTION OF HYDROGEN SULPHIDE ON PERMANGANATES. PART I. CALCIUM AND SILVER PERMANGANATES.

BY SARDAR MOHAMMAD AND GANGA SINGH AHLUWALIA.

Action of hydrogen sulphide on 1% solution of calcium and 0.5% solution of silver permanganates has been studied.

Dunnicliff and Nijhawan (*J. Chem. Soc.*, 1926, **129**, 1) have found that the action of hydrogen sulphide on a neutral solution of potassium permanganate yields hydrated manganese dioxide, sulphur, potassium sulphate and potassium dithionate. Excess of hydrogen sulphide converts manganese dioxide into manganese sulphide and decomposes potassium dithionate into potassium sulphate, thiosulphate and sulphur. The present work communicates the action of hydrogen sulphide on calcium and silver permanganates.

When a slow current of hydrogen sulphide is passed through 1% solution of calcium permanganate of tested purity, the purple solution deposits a dark brown precipitate. After a short time the solution becomes colourless and the precipitate still remains dark brown. Further passage of hydrogen sulphide results in the conversion of this precipitate into a sand-like precipitate of greyish colour. Finally the precipitate becomes pink due to the formation of manganous sulphide and the solution is found to be of yellow colour due to the formation of polysulphides. After passing the gas for several hours, even the polysulphides decompose giving a colourless solution. In order to determine the mechanism of the reaction, it was investigated at different stages.

EXPERIMENTAL.

Products of Reaction when Hydrogen Sulphide Water is added until the purple colour of the Calcium Permanganate just disappears.

To a calcium permanganate solution (1%, 100 c. c.) hydrogen sulphide water was added from a burette, until the purple colour of the permanganate just disappeared. The solution, containing the black precipitate, was filtered through a sintered glass crucible. The solution gave tests for sulphate and calcium readily. Thiosulphate was found to be present in traces. The formation of thiosulphate could be obviated if hydrogen sulphide water was added exactly to the decolorisation stage. Tri-, tetra-, and penta-thionates were found to be absent. The presence of dithionate was suspected since solutions gave small quantities of

sulphur dioxide on treatment with strong hydrochloric acid, which could be estimated by absorbing it in a standard solution of iodine.

Analysis of the Filtrate.—Calcium was estimated volumetrically after precipitating it as calcium oxalate. Sulphate was estimated gravimetrically. It was found that the amount of calcium recovered was less than that required for the formation of calcium sulphate. A portion of the filtrate was treated with potassium bromate and hydrochloric acid to oxidise any calcium dithionate, present. The free $(\text{SO}_4)''$ was precipitated as barium sulphate in cold (Mitchel, "Modern Methods of Chemical Analysis", p. 136). In the solution which was neutral, calcium was quantitatively accounted for as sulphate and dithionate (Ca in the precipitate : 40.33% and in the filtrate : 59.67%). Ca in the filtrate was accounted for as SO_4'' , 93.3% ; $\text{S}_2\text{O}_8''$, 6.7%.

The above experiments showed that only part of the calcium came in the filtrate as calcium sulphate and calcium dithionate.

The amount of calcium remained constant in the precipitate even if an experiment was repeated several times under identical conditions. In order to find out the way in which calcium is combined with the oxides of manganese, the precipitate was first treated with dilute solution of potassium hydroxide to remove co-ordinated sulphur compounds, if any (*cf.* Dunncliff and Kotwani, *J. Phys. Chem.*, 1931, **35**, 3214). The alkali extract did not contain any calcium or manganese. The precipitate was then treated with strong hydrochloric acid and the chlorine evolved was absorbed in U-tubes containing concentrated solution of potassium iodide. The liquid left over from this estimation was made slightly alkaline. The total manganese in it was removed as manganese sulphide and was estimated by the pyrophosphate method. Calcium present in the filtrate after the removal of Mn was estimated volumetrically after precipitating it as calcium oxalate. Estimation gave values of 7.2 : 1 for the molecular ratio of $\text{MnO} : \text{MnO}_2$ and 1.4 : 7.2 : 1 for the molecular ratio of $\text{CaO} : \text{MnO} : \text{MnO}_2$ (*vide* Table I, Expt. No. 3).

In order to elucidate the composition of the dark brown precipitate of the intermediate stage, the composition of the dark brown precipitate formed in the preliminary stages was also determined. In the first experiment (Table I, Expt. No. 1) the amount of hydrogen sulphide water added was one quarter of the hydrogen sulphide water, which was used for the intermediate stage. The estimation gave values of 1.6 : 1 : 3.66 for the molecular ratio of $\text{CaO} : \text{MnO} : \text{MnO}_2$. The ratio almost corresponds exactly to the ratio of the formula of the complex $2\text{CaO} \cdot \text{MnO} \cdot 3\text{MnO}_2$ (*vide* Table II). In the intermediate stages the

molecular ratio corresponds to the ratio of the formula of the complex compound $2\text{CaO} \cdot 9\text{MnO} \cdot \text{MnO}_2$. Complex compounds of potassium of similar structures have also been obtained by reducing potassium permanganate with hydrogen peroxide, sulphur dioxide, etc., and of some other metals by different methods (*cf.* Mellor, "Treatise in Inorganic Chemistry," Vol. XII, p. 274). By analogy the compound obtained in the intermediate stage would be called calcium manganous manganite and the compound obtained in the preliminary stage would be called calcium manganous trimanganite. (The authors have also detected the presence of similar compounds in the elementary stages in the reduction of potassium and ammonium permanganates by hydrogen sulphide. The work is under investigation).

More experiments were performed to investigate the formation of other complex compounds between the preliminary and the intermediate stages. Half the amount of hydrogen sulphide water that was required for the intermediate stage was added. The results are given in Table I, Expt. No. 2. The estimations give values of 1:1.56: 2.5 for the molecular ratio of $\text{CaO} : \text{MnO} : \text{MnO}_2$. From calculation it appears to be a mixture of the complex compounds formed in the preliminary and intermediate stages. The composition of the various complexes are given in Table II. The experiments were performed in duplicate.

In the preliminary stages precipitation of sulphur was not noticed due to an excess of the oxidising agent present. In the present case sulphylic acid S(OH)_2 may be considered as the precursor of sulphur acids formed in the reaction.

If the precipitate is allowed to remain in contact with dilute solution of potassium hydroxide for some hours, the alkali extract gives tests for sulphur acids, but calcium and manganese are found to be absent. This may be due to the presence of co-ordinated sulphur acids (Dunnicliff and Kotwani, *loc. cit.*) or probably it may be due to the oxidation of the adsorbed hydrogen sulphide in the presence of an alkali. This point is under investigation.

After the intermediate stage, further addition of hydrogen sulphide water makes the solution alkaline and results in thiosulphate formation.

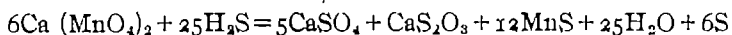
Analysis of the Products formed when Hydrogen Sulphide gas is passed through Calcium Permanganate Solution to produce Manganese Sulphide and Polysulphides.

Hydrogen sulphide was passed through calcium permanganate solution for one hour; the brown precipitate totally changed into manganese sulphide

and the filtrate became yellow due to the formation of polysulphides. Sodium bicarbonate was added and a stream of carbon dioxide was passed through the filtrate to remove excess of hydrogen sulphide and to decompose the polysulphides formed (*cf.* Bagster, *J. Chem. Soc.*, 1928, 2631). The solution obtained after filtration was made up to a known volume and was analysed for calcium and sulphur acids.

From Table II it appears that the value of $(\text{SO}_4)''$ obtained after bromination is accounted for as $(\text{SO}_4)''$ and $(\text{S}_2\text{O}_3)''$ present in the filtrate, thus showing the absence of the dithionate in the polysulphide and in the final stages, due probably to the hydrolysis of the dithionate to thiosulphate and sulphate (*cf.* Dunncliff and Nijhawan, *loc. cit.*). The thiosulphate formation is thus favoured by the increased reactivity of alkaline hydrolysis.

Expt. No. 3 (Table II) indicates the various products formed when hydrogen sulphide is passed into calcium permanganate solution for ten hours. The filtrate obtained is colourless. It is found that the values of sulphate and thiosulphate have still increased. The $(\text{SO}_4)''$ after bromination is again accounted for by $(\text{SO}_4)''$ and $(\text{S}_2\text{O}_3)''$. It is interesting to note that the values of calcium in the final stage are almost wholly accounted for as $(\text{SO}_4)''$ and $(\text{S}_2\text{O}_3)''$ present in the filtrate, and these values approximate to 5 molecules of calcium sulphate to 1 molecule of calcium thiosulphate. The results of the experiments of the last stage can be expressed by the equation,



Calculating from the experimental values the percentages of CaSO_4 (39.44%), CaS_2O_3 (8.7%) and MnS (62.6%), the molecular ratio comes to be 5:1:12.2.

The Action of Hydrogen Sulphide on Silver Permanganate.—On passing a slow current of pure hydrogen sulphide through a solution of silver permanganate (about 0.5%), a dark brown precipitate began to separate and the purple colour of the permanganate was discharged slowly. After the disappearance of the purple colour and the formation of dark brown precipitate, no further change was noticed in the reaction mixture.

The precipitate, obtained by passing an excess of hydrogen sulphide, contained sulphur and sulphides of silver and manganese. In the filtrate manganese was totally accounted for as sulphate. Found (Mn, 0.152 g. calc. from $(\text{SO}_4)''$: Mn, 0.151 g.).

Analysis of the Products formed when Hydrogen Sulphide Water is added just to remove the purple Colour of the Permanganate.

The filtrate obtained after the addition of hydrogen sulphide water gave

TABLE I.

Products of the precipitate at various stages of decomposition of calcium permanganate solution (1%).

No.	H ₂ S aq.	Ca (MnO ₄) ₂	CaO.	MnO ₂ .	Decomp. Ca(MnO ₄) ₂ .	Compound proposed.	Ratio CaO : MnO : MnO ₂ . Obs.	Calc.
1.	20 c.c.	100 c.c.	0.0556 g.	0.1480 g.	33.23%	2CaO. 9MnO ₂	1.6 : 1 : 3.66	1.58 : 1 : 3.67
2.	40	100	0.0668 [*]	0.0919	57.75	Probably a mixture of the two compounds.]]	
3.	80	100	0.0848	0.4600	*100	2CaO. 9MnO ₂	1.4 : 7.2 : 1	1.3 : 7.3 : 1

* 100% decomposition indicates stage at which the purple colour of the permanganate just disappeared.

TABLE II.

The polysulphide and the final stage.

Ca(MnO₄)₂ = 50 c.c. containing 0.4817 g. per 50 c.c. water.

No.	H ₂ S gas bubbled.	Mn*.	Ca.	*(SO ₄)* cold.	(S ₂ O ₃)*.	(SO ₄)* after bromination.	(S ₂ O ₃)* in terms of (SO ₄)*.	Total (SO ₄)* due to S ₂ O ₃ and free (SO ₄)*.
1.	1 hour	0.1906 g.	0.069 g.	0.1205 g.	0.0196 g.	0.1531 g.	0.0336 g.	0.1541 g.
2.	1	0.1906	0.069	0.1203	0.0196	0.1533	0.0336	0.1539
3.	10	0.1906	0.069	0.1341	0.0308	0.1868	0.0528	0.1869

*(Mean value).

TABLE III.

Silver permanganate used = 6.5095 g. per litre.

No.	AgMnO ₄ used.	I	II	III	IV	V	VI	VII	VIII	IX	X
1.	400 c.c.	0.4663 g.	(SO ₄) ²⁻ pptd. (cold).	(SO ₄) ²⁻ after bromination.	Mn.	Ag.	(SO ₄) ²⁻ corresponding to Mn.	Diff. bet. Cols. II and III, i.e. (SO ₄) ²⁻ in terms of (S ₂ O ₈) ²⁻	Silver corresponding to Ag-dithionate from Col. VII.	(SO ₄) ²⁻ corresponding to Ag from Col. V.	The sum of the values from Col. VI, VII and IX.
2.	400	0.4681		0.4850	0.1930 g.	0.3100 g.	0.3368 g.	0.0182 g.	0.0205 g.	0.1287 g.	0.4837 g.
					0.1928	0.3106	0.3364	0.0171	0.0192	0.1295	0.4830

tests for silver, manganese and sulphate. Thiosulphate was not detected, though the solution evolved a small amount of sulphur dioxide with hydrochloric acid. The solution remained neutral at this stage and also after further addition of hydrogen sulphide water. Complete quantitative analysis of the solution showed that silver (estimated as AgCl) was accounted for as (SO₄)²⁻ and (S₂O₈)²⁻, while Mn (estimated as Mn₂P₂O₇ after the removal of silver) as sulphate only. The results are embodied in Table III.

To elucidate the composition of the products formed in the precipitate, different amounts of hydrogen sulphide water were added and the precipitates obtained were analysed for the oxides of silver and manganese. Table IV embodies the results of the various experiments. 100% Decomposition of the silver permanganate indicates the stage at which the purple colour of the permanganate just disappeared by the slow addition of hydrogen sulphide water. The reaction was not complete at this stage. The presence of silver sulphide and manganese sulphide in traces did not permit determination of the exact composition of the precipitate at this stage.

TABLE IV.

AgMnO_4 decomposed	Ag_2O	MnO	MnO_2	AgMnO_4 decomposed.	Ag_2O	MnO	MnO_2
29.42%	0.0333 g.	0.0264 g.	0.0357 g.	51.49	0.0574 g.	0.0049 g.	0.0588 g.
33.76	0.0450	0.0207	0.0443	72.65	0.0888	0.0218	0.0718
35.1	0.0233	0.0224	0.0435	100.00	0.2107	0.1149	0.0008

Table IV shows that there is a gradual change in the beginning in the amounts of the products formed. When the decomposition is about 35% (just like the decomposition of calcium permanganate) there is a sudden change in the amounts of the products formed and the decomposition of the precipitate corresponds to the formula $\text{Ag}_2\text{O} \cdot 3\text{MnO} \cdot 5\text{MnO}_2$. The formation of the products after this stage becomes irregular until the compound is changed into silver and manganese sulphides.

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Received April 2, 1941.

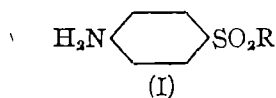
CHEMOTHERAPY OF BACTERIAL INFECTIONS.

PART III, N¹-β-PHENYLETHYLSULPHANILAMIDES.*

BY P. L. NARASIMHA RAO.

In order to throw light on the so-called specificity of antibacterial action of a drug to its chemical structure, and also to discover a sulphanilamide drug for use in enteric diseases, some N¹-β-phenylethylsulphanilamides have been synthesised.

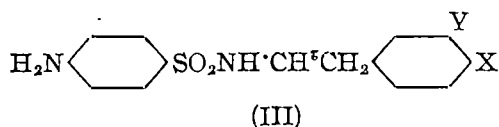
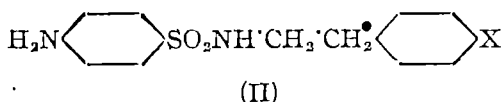
A striking fact about sulphanilamide is its high curative ability in a number of resistant bacterial infections, *i.e.* its polyvalent action which tends to increase in specificity of the compounds obtained by proper substitution at N¹, towards one type of bacteria. It would, however, appear premature from the meagre experimental data available to propound any theory connecting the substituent group 'R' (in I) to the characteristic



bacterial morphology or aetiology of their infections, much less to determine beforehand what "R" must be, so that the product may possess any desired "specificity". In the present investigation, which was undertaken with a view to finding out an effective chemotherapeutic agent for use in enteric diseases, an attempt has been made to see whether the nature of the substituent 'R' could be correlated with the peculiar demands of these infections as evinced by their aetiological analysis. It is known (*Compt. rend. Soc. Biol.*, 1937, **125**, 796; *Compt. rend.*, 1937, **204**, 1759) that enteric bacteria strictly confine themselves to intestinal tracts which are rendered in many cases hypothermic and alkaline. Shiga organisms, besides elaborates an enterotropic endotoxin (showed by Flexner and Sonne strains) and a neurotropic endotoxin which get absorbed by the intestinal walls. From a careful analysis of the works of Kolmer and Rule (*Proc. Soc. Expt. Biol. & Med.*, 1939, **40**, 23) and Levaditi and Vaisman (*Compt. rend. Soc. Biol.*, 1938, **128**, 463; 1939, **131**, 33) it should be inferred that sulphonamides though possessing definite antiendotoxic and antibacterial action fail to give any favourable result against the endotoxin. It is, therefore, imperative to take into

* Presented before the meeting of the Society of Biological Chemists (India) on 28th September, 1940.

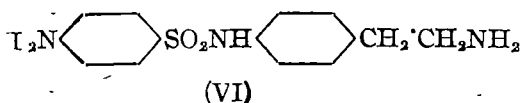
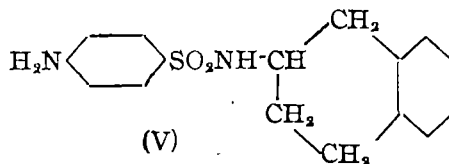
account this important fact in devising any therapeutic agent. In order to control the absorption of this exotoxin into the blood, and to effect a cure of Shiga infections, the enteric walls should be rendered less permeable *i.e.* the drug should be endowed in addition with vasoconstricting action. The usual vasoconstrictors being compounds of the β -phenylethylamine class, it occurred to the author that the specifying group R in (I) for Shiga infections may belong to this class. Accordingly some N¹- β -phenylethylsulphanilamides (II, X=H, OH, OMe, NH₂ and NO₂; III, X=Y=OMe) have been prepared for pharmacological examination. It may be pointed



out in this connection that derivatives of phenylethylamine carboxylic acids like phenylalanine and tyrosine give active products against streptococci.

There is another important peculiarity of this group that also demands attention in this connection *viz.* the hypothermic factor (Olitzi and Avinery, *Brit. J. Exptl. Path.*, 1937, **18**, 316). In order to overcome this *ac*-tetrahydro- β -naphthylamine, a unique compound combining in itself powerful vasoconstrictor action and calorising capacity has been utilised (*cf.* V).

However, as the nature of the pressor action has been normally assumed to be dependent upon the presence or liberation *in vivo* of a free amino (or imino) group in phenylethylamine, it appeared desirable also to prepare compounds having such a grouping, while being at the same time fused at N¹-nitrogen of sulphanilamide *e.g.* (VI).



The results of the pharmacological examination of these compounds will be published in due course.

EXPERIMENTAL.

In the following experiments yields of products should be taken as varying from 80 to 100 % unless explicitly stated.

*N*¹- β -Phenylethylacetylsulphanilamide, obtained by interacting β -phenylethylamine (6 g.) and freshly prepared *p*-acetylaminobenzene sulphonyl chloride (12 g.) in the usual way in presence of sodium hydroxide (20 c.c. of 2.5*N*), crystallised from alcohol in lustrous lumps, m.p. 126°. (Found: N, 8.9. $C_{16}H_{18}O_3N_2S$ requires N, 8.81 per cent).

*N*¹- β -Phenylethylsulphanilamide.—The above acetyl compound (8 g.) was boiled with hydrochloric acid (10 %, 60 c.c.) under reflux for 25 minutes. The clear solution on cooling deposited glistening plates of the hydrochloride of the base, m.p. 225°. (Found: N, 9.1. $C_{14}H_{17}O_2N_2ClS$ requires N, 8.96 per cent). The free base obtained by decomposing the above salt with ammonia crystallised from alcohol in colourless, glistening, elongated plates, m.p. 143°. (Found: N, * 10.2. $C_{14}H_{16}O_2N_2S$ requires N, 10.15 per cent).

*N*¹-(4-Methoxy- β -phenylethyl)-acetylsulphanilamide, prepared in the usual manner, crystallised from alcohol (charcoal) in stout prism-like crystals, m.p., 157°. (Found: N, 7.9. $C_{17}H_{20}O_4N_2S$ requires N, 8.1 per cent).

*N*¹-(4-Methoxy- β -phenylethyl)-sulphanilamide.—The above acetyl compound was boiled with excess of 10% hydrochloric acid for about 1½ hours. On cooling, the solution deposited colourless plates of the hydrochloride, m.p. 218-9° (decomp.). (Found: Cl, 10.5. $C_{15}H_{18}O_3N_2ClS$ requires Cl, 10.36 per cent). The free base was obtained by treating the salt with ammonia and was purified by crystallisation from alcohol. It separated in shining thick aggregates of rods, m.p. 149°. (Found: N, 9.2. $C_{13}H_{18}O_3N_2S$ requires N, 9.15 per cent). Refluxing the amine with concentrated hydrobromic acid solution for 3 hours and just basifying the product with ammonia, a colourless amorphous product, m.p. about 185° (decomp.), sparingly soluble in hot alcohol, was obtained. It gave a violet colouration with ferric chloride. (Found: N, 9.3. $C_{14}H_{16}O_3N_2S$ requires N, 9.59 per cent). (The experiments with tyramine and other β -phenylethylamine alkaloids are reserved for a future communication).

*N*¹-(3:4-Dimethoxy- β -phenylethyl)-sulphanilamide.—The crude acetyl compound, obtained in the usual way, after washing was directly hydrolysed by refluxing with hydrochloric acid (10%, 100 c.c.) for 1 hour. The clear

and somewhat concentrated solution was made just alkaline with ammonia under cooling. The pale yellow product, thus obtained, was purified by twice crystallisation from 50% alcohol (charcoal) as colourless plates, m.p. 126-27°. (Found : N, 8.4. $C_{16}H_{20}O_4N_2S$ requires N, 8.33 per cent).

*N*¹-(4-Nitro- β -phenylethyl)-acetylsulphanilamide, prepared from the corresponding nitroamine by the general method, was purified by successive crystallisations from 80 % acetic acid and alcohol. It separated in shining spangles or thick plates from alcohol, m.p. 183-84°. (Found : N, 11.4. $C_{16}H_{17}O_5N_3S$ requires N, 11.57 per cent).

*N*¹-(4-Nitro- β -phenylethyl)-sulphanilamide.—The above acetyl compound was boiled with ten times of hydrochloric acid (10%) for $\frac{1}{2}$ hour. The hydrochloride that separated on cooling decomposed at about 202° with melting. The free base obtained after treatment of the solution with ammonia, crystallised from alcohol in pale yellow prismatic needles, m.p. 207°. (Found : N, 13.1. $C_{14}H_{15}O_4N_3S$ requires N, 13.08 per cent).

*N*¹-(4-Amino- β -phenylethyl)-sulphanilamide was obtained by the reduction of the above nitro compound using tin and hydrochloric acid. (The reduction of acetyl derivative of the nitro compound was not satisfactory). A mixture of the nitro compound (5 g.), tin foil (5 g.), water (15 c.c.) and hydrochloric acid (30 c.c.) was heated on the water-bath till the nitro compound went into solution. After dilution with water and removal of tin as sulphide in the usual way, the solution was somewhat concentrated and just basified with ammonia. The diamine crystallised from alcohol in colourless, prismatic plates, m.p. 154-55° (Found : N, 14.5. $C_{14}H_{17}O_2N_3S$ requires N, 14.42 per cent). It is somewhat unstable as it turns pinkish on heating in alcoholic solution. The di-acetate, m.p. 230°, separated from alcohol in silky plates or feathery needles. (Found : N, 11.4. $C_{18}H_{21}O_4N_3S$ requires N, 11.2 per cent).

dl-*N*¹-(ac-Tetrahydro- β -naphthyl)-acetylsulphanilamide, obtained from the appropriate amine and sulphochloride in the usual way, crystallised from alcohol in colourless prismatic needles or columns, m.p. 190-91°. (Found : N, 8.2. $C_{18}H_{20}O_3N_2S$ requires N, 8.14 per cent).

dl-*N*¹-(ac-Tetrahydro- β -naphthyl)-sulphanilamide.—The above acetyl compound (10 g.) was refluxed for 20 minutes with sodium hydroxide (2.5 N, 50 c.c.), and the solution treated with excess of ammonium chloride. The amine, thus obtained, crystallised from boiling alcohol in prismatic needles, m.p. 163°. (Found : N, 9.3. $C_{16}H_{18}O_2N_2S$ requires N, 9.27 per cent). The hydrochloride which turned red on keeping, crystallised from hot hydrochloric acid (10%) in silky plates, m.p. 204-6° (decomp.). (Found : Cl, 10.3. $C_{16}H_{19}O_2N_2ClS$ requires Cl, 10.49 per cent).

N-Benzoyl-β-(4-aminophenyl)-ethylamine, required for the following experiments, was conveniently prepared from the corresponding nitro compound by reduction with sodium sulphide (cf. Barger and Walpole, *J. Chem. Soc.*, 1909, **95**, 1722). The nitro compound (24.6 g.), dissolved in hot alcohol, was gradually treated with a concentrated aqueous solution of sodium sulphide crystals (27 g.) and the mixture refluxed for 3 hours on a steam-bath. After removal of alcohol and dilution with water, the separated solid was collected, washed with water and twice crystallised from ethyl acetate, yield 20 g. of pure product.

N¹-(4-β-Benzoylaminoethylphenyl)-acetylsulphanilamide was obtained from the above amine using pyridine as a condensing agent. The product was washed free of pyridine and crystallised from alcohol. The acetylbenzoyl compound separated in fine crystals, m.p. 198-200°. (Found : N, 9.8. $C_{23}H_{23}O_4N_3S$ requires N, 9.61 per cent).

N¹-(4-β-Aminoethylphenyl)-sulphanilamide.—The above derivative (15 g.) was heated for a short time with sodium hydroxide solution (2.5 N, 50 c.c.) when a clear solution resulted. The hot liquid gradually deposited shining leaflets of the sodium derivative of the diamine. It was collected and decomposed by adding an aqueous solution of ammonium chloride. The precipitated solid was crystallised by dissolving in hot pyridine and diluting with hot alcohol. The diamine separated in rosettes of slender silky plates, m.p. 243°. (Found : N, 14.4. $C_{14}H_{17}O_2N_3S$ requires N, 14.42 per cent). The dihydrochloride decomposed at about 210°. The diacetyl derivative, prepared in the usual way, crystallised from alcohol in shining silky prismatic plates, m.p. 223°. (Found : N, * 11.2. $C_{18}H_{21}O_4N_3S$ requires N, 11.2 per cent).

My grateful thanks are due to Prof. P. C. Guha, D.Sc., F.N.I., for his keen interest in this investigation.

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Received March 12, 1941.

* Micro-analysis.

ADSORPTION OF POLYBASIC ORGANIC AND INORGANIC ACIDS. DISCONTINUITIES IN ADSORPTION PROCESS FROM SOLUTIONS OF SUGAR CHARCOAL.

BY KRSHO DASS JAIN AND J. B. JHA.

Adsorption of a few polybasic acids, both organic and inorganic, by sugar charcoal has been investigated. Results indicate a discontinuous nature of the process.

In our previous paper (*J. Indian Chem. Soc.*, 1940, 17, 85) we found that the mode of adsorption of acids by sugar charcoal depended on the constitution of acids. In the case of monobasic acids we found no deviation from the general laws, while in the case of di- and tribasic acids, the adsorption curve was somewhat of a periodic type.

In the following work we have further studied some di- and tribasic organic and inorganic acids and found confirming results.

EXPERIMENTAL.

The same procedure with the same sugar charcoal was followed as was done in the previous work. The bottles were allowed to stand for 40 hours in case of fumaric and maleic acids, and for 18 hours in the case of inorganic acids at 30° (room temperature).

The results of fumaric and maleic acids are shown in Fig. 1 and Table I, and those of phosphoric, chromic and sulphuric acids in Fig. 2 and Table II.

TABLE I.
Organic acids.

Adsorption of acids by 0.5 g. of charcoal from 100 c.c. aqueous solution.

Fumaric acid.

C ₀ .	C _e .	X.	X/m.	Log C _e .	Log X/m.
0.1292	0.1077	0.0215	0.0430	1.0324	2.6335
0.1266	0.1035	0.0231	0.0462	1.0152	2.6646
0.1241	0.1019	0.0222	0.0444	1.0081	2.6474
0.1215	0.0994	0.0221	0.0442	2.9975	2.6454
0.1189	0.0961	0.0228	0.0456	2.9825	2.6590
0.1163	0.0944	0.0219	0.0438	2.9753	2.6415
0.1137	0.0886	0.0251	0.0502	2.9477	2.7007

TABLE I (contd.).

Maleic acid.					
C ₀ .	C _a .	X.	X/m.	Log C _a .	Log X/m
0'1292	0'1143	0'0149	0'0298	1'0582	2'4742
0'1266	0'1110	0'0156	0'0312	1'0454	2'4942
0'1241	0'1093	0'0148	0'0296	1'0390	2'4728
0'1215	0'1068	0'0147	0'0294	1'0290	2'4683
0'1189	0'1035	0'0154	0'0308	1'0149	2'4886
0'1163	0'1027	0'0136	0'0272	1'0118	2'4346
0'1137	0'1019	0'0118	0'0236	1'0082	2'3729
0'1111	0'0986	0'0125	0'0250	2'9939	2'3979

TABLE II.

Inorganic acids.

Adsorption of acids by 0.5 g. of charcoal from 100 c.c. aqueous solution.
Orthophosphoric acid.

C ₀ .	C _a .	X.	X/m	Log C _a .	Log X/m
1'4391	1'4300	0'0091	0'0182	0'1553	2'2601
1'4103	1'4025	0'0078	0'0156	0'1468	2'1931
1'3959	1'3933	0'0026	0'0052	0'1460	3'7160
1'3815	1'3566	0'0249	0'0498	0'1324	2'6972
1'3527	1'3383	0'0144	0'0288	0'1265	2'4594
1'3239	1'3016	0'0223	0'0446	0'1145	2'6493
1'2952	1'2741	0'0211	0'0422	0'1052	2'6253
1'2376	1'2283	0'0093	0'0186	0'0892	2'2695
1'2088	1'1916	0'0172	0'0344	0'0761	2'5366
1'1512	1'1366	0'0146	0'0292	0'0555	2'4654

Chromic acid.

2'8500	2'8296	0'0204	0'0408	0'4517	2'6107
2'7930	2'7694	0'0236	0'0472	0'4424	2'6739
2'7645	2'7292	0'0353	0'0706	0'4361	2'8488
2'7330	2'7092	0'0268	0'0536	0'4330	2'7292
2'6790	2'6490	0'0300	0'0600	0'4231	2'7782
2'6220	2'5486	0'0734	0'1468	0'4062	1'1668
2'5650	2'4884	0'0766	0'1532	0'3960	1'1853
2'4795	2'4683	0'0112	0'0224	0'3923	2'3502
2'3940	2'3279	0'0661	0'1322	0'3670	1'1212
2'2515	2'2479	0'0039	0'0078	0'3516	3'8921

TABLE II (contd.).

Sulphuric acid.					
C_0 .	C_a .	X .	X/m .	$\text{Log } C_a$.	$\text{Log } X/m$.
1.9248	1.9110	0.0138	0.0276	0.2812	2.4409
1.8863	1.8835	0.0028	0.0056	0.2749	3.7482
1.8670	1.8491	0.0179	0.0358	0.2669	2.5539
1.8478	1.8425	0.0053	0.0106	0.2653	2.0253
1.8093	1.8010	0.0083	0.0166	0.2555	2.2201
1.7708	1.7598	0.0110	0.0220	0.2455	2.3424
1.6938	1.6910	0.0028	0.0056	0.2282	3.7482
1.6553	1.6504	0.0049	0.0098	0.2177	3.9912
1.6168	1.5948	0.0220	0.0440	0.2028	2.6435
1.5783	1.5673	0.0110	0.0220	0.1951	2.3424

The results in Table III give an idea about the shape of the curves.

TABLE III.

Molar conc. at the max. and min. pts on the curves.	Diff. in molar conc. between two max. and min. pts.	Molar conc. at the max. and min. pts. on the curves.	Diff. in molar conc. between two max. and min. pts.
Fumaric.		Maleic.	
0.000806	—	0.00095	—
0.00085	0.00004	0.00092	0.00003
0.00083	0.00002	0.00089	0.00003
0.00081	0.00002	0.000875	0.000015
0.00076	0.00005		
Oxalic.		Malonic.	
0.0154	—	0.0278	—
0.0152	0.0002	0.0263	0.0015
0.0148	0.0004	0.0248	0.0015
0.0146	0.0002	0.0236	0.0012
0.0142	0.0004	0.0221	0.0515
0.0136	0.0006		
0.0130	0.0006		
Succinic.		Phthalic.	
0.0243	—	0.00191	—
0.0231	0.0012	0.00181	0.00010
0.0218	0.0013	0.00166	0.00015
0.0194	0.0024	0.00161	0.00005
0.0168	0.0026		

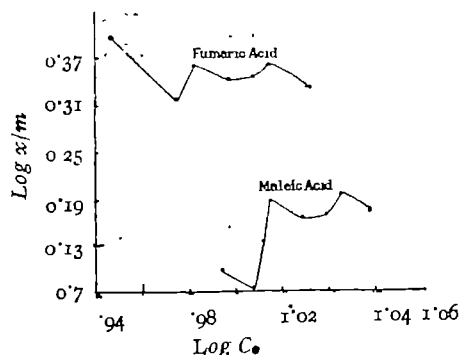
TABLE III (contd.).

Molar conc. at the max. and min. pts. on the curves.	Diff. in molar conc. between two max. and min. pts.	Molar conc. at the max. and min. pts. on the curves.	Diff. in molar conc. between two max. and min. pts.
Chromic.		Citric.	
0.02313	—	0.0121	—
0.02296	0.00017	0.0101	0.0020
0.02109	0.00087	0.0096	0.0005
0.02091	0.00018	0.0089	0.0007
0.01973	0.00118	0.0084	0.0005
		0.0078	0.0006
		0.0073	0.0005
Orthophosphoric.		Sulphuric.	
0.01422	—	0.01942	—
0.01384	0.00038	0.01887	0.00055
0.01365	0.00019	0.01880	0.00007
0.01328	0.00037	0.01837	0.00043
0.01253	0.00075	0.01795	0.00042
0.01216	0.00037	0.01684	0.00111
Sodium hydrogen oxalate.		Sodium hydrogen succinate.	
0.0092	—	0.0102	—
0.0088	0.0004	0.0092	0.0010
0.0083	0.0005	0.0087	0.0005
0.0079	0.0004	0.0082	0.0005
0.0074	0.0005	0.0077	0.0005
0.0070	0.0004		
Potassium hydrogen phthalate.			
		0.0110	—
		0.0098	0.0012
		0.0094	0.0004

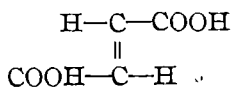
DISCUSSION.

In our previous work the adsorption was found to be greatly influenced by the basicity of acids. Thus we found that the adsorption curve in the case of monobasic acids is invariably a straight line while in the case of polybasic acids a zigzag curve is obtained which seems to be periodic.

FIG. 1.



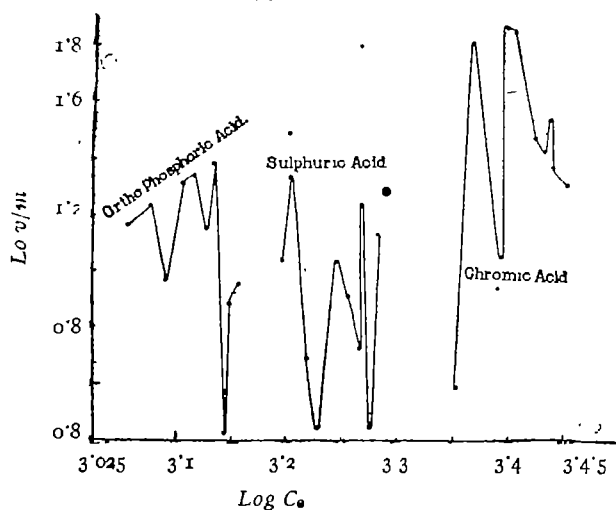
Further in the case of fumaric and maleic acids we find the curves to be similar, the only difference being the vertical displacement. In the case of fumaric acid which has the structure



the curve is displaced upwards.

There is no other difference between the two curves. The fumaric and maleic acids are similar in all respects except that in fumaric acid the COOH groups are in the opposite sides and in the maleic acid they are on the same side of the double bond.

FIG 2.



Further in the study of some di- and tribasic acids and their bi-salts, we obtain the same zigzag curves, showing some relations in their constitution.

In each case (Table III) the differences between the equilibrium molar concentrations at the maxima and the minima points are multiple, although in some cases it is not so. This may be due to the fact that the points might be displaced from their right place. It is just possible that if the points were taken more closely a definite periodic curve might be obtained.

The authors are thankful to Professors H. Krall and B. L. Vaish for their kind guidance and advice in this work.

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Received February 22, 1941.

DETERMINATION OF COPPER IN COUNTRY SPIRITS.

By H. D. SURI, GURCHARAN SINGH AHLUWALIA AND H. B. DUNNICLIFF.

A method has been worked out for the estimation of copper in country spirits by use of the reagent diethyl dithiocarbamate, which has been found useful specially in cases where the percentage of copper or the quantity of spirit submitted for test is very small.

Country spirits, *i.e.* potable spirits made from *gur*, molasses, mahua etc., with or without flavouring, are examined for contamination with metals such as copper, iron, lead or zinc which may be present as a result of using metallic plant and storage vessels in the distilleries. As copper stills and pipes are mostly used, contamination with this metal is commonly found both in plain and spiced liquors. A permissible maximum limit of one quarter grain per gallon of spirit has been prescribed for copper (*vide* C. H. Bedford, "Technical Excise Manual," p. 50).

The determination of copper is generally carried out by dissolving the ash from 20 ml. of spirit in a few drops of concentrated hydrochloric acid and removing any iron present by ammonium hydroxide. After acidifying the ammoniacal filtrate with dilute acetic acid, a few drops of freshly prepared potassium ferrocyanide are added and the copper estimated by matching the intensity of the reddish brown colour produced against known standards.

This method is not satisfactory because (a) the colour produced in acid solution tends to change from a reddish to an earthy brown, and (b) reliable results cannot be obtained when the quantity of copper is less than 0.1 grain per gallon of spirit.

Several reagents were tested for the colorimetric estimation of copper, *e.g.*, dimethylglyoxime (Clark and Jones, *Analyst*, 1929, **54**, 333), potassium iodide (Dunncliff and Ram, *Kolloid Z.*, 1926, **38**, 168), pyridine and potassium thiocyanate (Spacu, *Bull. Soc. Stiinte Cluj*, 1922, **1**, 352), sodium diethyldithiocarbamate (Callan and Henderson, *Analyst*, 1929, **54**, 650), rubeanic acid (Allport and Skrimshire, *Quart. J. Pharmacol.*, 1932, **5**, 461), salicylaldoxime (Astin and Riley, *J. Chem. Soc.*, 1933, 314), and α -benzoin oxime Gruzewaka and Russel, *Compt. rend. Soc. Biol.*, 1936, **121**, 289).

In the experience of the authors the potassium ferrocyanide method as described by Scott and Furman ("Standard Methods of Chemical Analysis", 5th Ed., Vol. I, p. 377), slightly modified, is suitable when the concentration of copper exceeds 0.1 grain per gallon of spirit and the sodium

diethyldithiocarbamate method. (*Analyst*, 1939, **64**, 339) when the copper is in traces or when the quantity of spirit submitted for test is very small.

EXPERIMENTAL.

Preparation of the Sample.—To 20 ml. of the spirit under test in an evaporating dish, add 1 ml. of dilute sulphuric acid (10 per cent. w/w). Evaporate almost to dryness on a water-bath (heating gently in the beginning) and ignite the residue over a clear flame to eliminate the sulphuric acid. Cool, dissolve the residue in 2 ml. of distilled water, add 2-3 drops of aqua regia and evaporate to dryness on a water-bath. Dissolve the residue in distilled water (removing if necessary iron by double precipitation for the ferrocyanide method only) and make up the volume to 25 ml. Determine copper by either of the two methods detailed below depending upon the quantity of copper present.

The solutions are essentially the same as those given by Scott and Furman (*loc. cit.*) except that the standard copper solutions are made up as follows:—

Solution A.—Dissolve 1.119 g. of A. R. copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled water and dilute to 1,000 ml. (1 ml. = 0.0002845 g. or 0.00439 grains of copper). This solution is retained as a stock solution.

Solution B.—It is made up immediately before use by taking 10 ml. of this solution and diluting to 100 ml. (1 ml. = 0.0002845 g. or 0.00439 grain copper).

Procedure.—Measure 0.25 ml. of freshly prepared 4 % ammonium nitrate solution into a Nessler tube of 50 ml. capacity and then add 25 ml. of the neutral solution of the assay prepared as directed above. Dilute to 50 ml. Simultaneously prepare in the same way four comparison tubes to which is added from a burette 1.0, 2.0, 2.5 and 3.0 ml. of standard solution B respectively. Make up the volume in each tube to 50 ml. Mix thoroughly and compare the colour with that of the assay by viewing the liquid from the top against a white surface (or use a colorimeter). The temperature of the solutions should be kept below 20°.

The number of ml. of standard solution B, required by the comparison tube, which matches with the colour of the solution of the sample under test, multiplied by 0.1, gives the weight of copper in grains per gallon in the sample of spirit.

Sodium Diethyldithiocarbamate Method.

The reagent gives a golden brown colour in acid, ammoniacal or neutral solutions and is used for the colorimetric determination of copper

when the spirit contains less than 0.1 grain of the metal per gallon of spirit.

Special Solutions : (i) Standard copper solution ; same as above.

(ii) A 0.1% solution of sodium diethyldithiocarbamate $(C_2H_5)_2N \cdot CSSNa$ in distilled water. This reagent keeps well for several weeks in an amber-coloured bottle.

Procedure : (a) *Without Extraction*.—In a 50 ml. Nessler tube, take 10 ml of the neutral solution of the assay from which iron has not been removed. Add 2 g. of citric and 10 c.c. of (10% v/v) ammonia, or more until $pH = 9$. Make up to 50 ml. with distilled water.

Prepare a series of standard comparison solutions, each containing in 50 ml., 2 g. of citric acid, and ammonia solution of $pH 9$ together with increasing amounts of copper (i.e., 0.1, 0.4, 0.6, 0.8 and 1.0 ml. of standard copper solution B).

The test solutions and standards should be water-white.

Cool all solutions to 20° and to each add 2 ml. of diethyldithiocarbamate and match the test solution against the standard comparison solutions.

(b) *Extraction Method*.—Extract immediately the copper organo-metallic compound produced as in (a), with four successive portions (2.5 ml. each) of carbon tetrachloride and compare the colour of the solution so obtained in a colorimeter with the extracts of standard solutions similarly prepared. Chloroform may be used but carbon tetrachloride is better as it is almost insoluble in water and forms clearer solutions which separate quickly.

The number of ml. of standard solution B used in the tube having the same shade as that of the sample, multiplied by 0.25 gives the weight of copper in grains per gallon of this sample.

A blank experiment must be carried out with the same quantities of the reagents to detect copper contamination in any of them.

THE FATTY OIL FROM THE SEEDS OF *SOLANUM INDICUM*, LINN.

By S. V. PUNTAMBEKAR AND S. KRISHNA.

The oil from the seeds of *Solanum indicum*, Linn. consists of the glycerides of lauric, palmitic, stearic, arachidic, oleic and linoleic acids together with the phytosterols, sitoaterol and carpesterol, and a hydrocarbon of high molecular weight and of m.p. 66-67°.

Solanum indicum, Linn. (N.O. *Solanaceae*) known as Vrihati in Sanskrit and Birhatta in Hindi is a much branched under-shrub found throughout India and is particularly plentiful in the forests of Madras Province. The plant is an important drug of the Ayurvedic system of medicine, its roots being included among the ten important roots (dasamula) used for bronchitis, asthma and difficult parturition (Watt, "Dictionary of the Economic Products of India", Vol. VI, IIIA, p. 258). The fruit is a berry 0.3—0.35" in diameter, yellow when ripe and contains several small seeds which yield a yellowish orange fatty oil. The oil is also considered to possess medicinal properties.

A few physical and chemical constants of the fatty oils from the seeds of the allied species *S. melongena*, Linn., *S. mammosum*, Linn., *S. surinamense*, Steud (*Olien und Vetten*, 1919, 4, 417) and *S. lycopersicum* (Jemieson and Bailey, *Ind. Eng. Chem.*, 1919, 11, 850; Rabak, *Chem. News*, 1917, 117, 100) have been previously recorded. But only recently the fatty oils obtained from the seeds of *S. xanthocarpum*, Schrad and Wendle (Gupta and Dutt, *J. Indian Chem. Soc.*, 1937, 14, 367) and from the seeds of *S. nigrum*, Linn. (Pendse, *ibid.*, 1937, 14, 367) have been examined in some detail and shown to consist of the glycerides of palmitic, stearic, oleic and linoleic acids. Our examination of the fatty oil from the seeds of *S. indicum* Linn., the results of which are recorded below, has shown that besides the glycerides mentioned above, the oil contains small percentages of the glycerides of lauric and arachidic acids.

EXPERIMENTAL

The air-dried berries of *S. indicum* were received from the Divisional Forest Officer, Lansdowne Forest Division, Lansdowne, U.P., and were found to consist of 35% fruit shell and 65% seeds. The powdered seeds on extraction with petroleum ether yielded 10.1% of a pale yellow fatty oil having the constants recorded in Table I.

TABLE I.
Chemical and physical constants.

FATTY OIL.					
Consistency	... Thin	Sap. value	... 177.6		
Rotation $[\alpha]_{D}^{25^{\circ}}$... +0.5	Acid value	... 17.8		
		Acetyl value	... 44.4		
Sp. gr. at 15.5°	... 0.9156	Unsaponifiable matter	... 2%	<div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 10px;">{</div> <div> Carpestrol, 0.15% Residual matter, 1.8% </div> </div>	
Refrac. index at 15.5°	1.4671				
Iodine value (Hanus)	... 121.5				
MIXED ACIDS.					
Mean M.W.	... 293.1	Saturated acids	... 15.5%		
Iodine value (Hanus)	... 123.0	Unsaturated acids	... 84.5%		

Composition of the Mixed Fatty Acids

The oil (200 g.) was saponified with alcoholic sodium hydroxide. After distilling off the alcohol the resultant soap was dissolved in water and the mixed acids liberated by the addition of concentrated hydrochloric acid. The acids were washed with warm water and neutralised with 10% sodium hydroxide. The soap solution was concentrated by evaporation on a water-bath, incorporated with washed filter paper pulp and the resulting mass was dried, powdered and extracted with ether in a Soxhlet to remove the unsaponifiable matter. The mixed acids (142 g) were liberated from the residual soap, purified in the usual manner and were separated into solid and liquid acids by the well known Twitchell's lead salt-alcohol method (*Ind. Eng. Chem.*, 1921, 13, 806).

Acids.	Net weight.
(S) Solid	23 g.
(S') Solid	1.2
(L) Liquid	117.8

Solid Acids (S).

The solid acids (23 g.) were converted into methyl esters in the usual manner with 3% methyl alcoholic hydrochloric acid. After distilling off methyl alcohol the esters were washed with saturated salt solution, 5% sodium carbonate and finally with distilled water. After drying under vacuum 23 g. of the esters were distilled at 6 mm. into the following fractions (TABLE II).

TABLE II.

Fractions.	B.p.	Mean M.W.	Net wt.	Component methyl esters					
				Laurate.	Palmitate.	Stearate.	Arachidate.		
S ₁	up to 175°	248·7	1·90 g	0·72	1·18		
S ₂	175-180°	274·4	2·18	...	1·84	0·34	...		
S ₃	180-185°	275·7	4·06	...	3·23	0·83	...		
S ₄	185-187°	285·9	5·12	...	2·21	2·91	...		
S ₅	187-192°	289·9	3·14	...	0·91	2·23	..		
S ₆	192-205°	304·6	1·80	1·38	0·42		
Residue	...	Unpolymerised		1·00	1·00		
		Polymerised*		1·94		
Loss	0·86		
Total	23·00	0·72	9·37	8·69	1·42		
% Esters un- polymerised and distilled (20·2g.)				...	100·00	3·57	46·39	43·00	7·04

All these fractions were separately saponified, the corresponding acids were liberated and these were fractionally crystallised from acetone to isolate the individual acids in the usual manner.

Acids from fraction S₁ had a mean M.W. of 234·7. On twice crystallising from dilute acetone a product melting at 59-61° (Mean M.W. 258) was obtained. Mixed with pure palmitic acid, the m.p. was raised to 61-62°. The fraction, therefore, appeared mostly to consist of palmitic with some lauric acid. That it contained lauric acid is proved by the fact that this acid has been isolated from solid acids (S') as described later.

Acids from fractions S₂, S₃, S₄ and S₅ were separately obtained and fractionally crystallised from acetone. They were found to consist of palmitic and stearic acids. Fractions S₂ and S₃, on crystallisation, yielded almost pure palmitic acid (m.p., 61-62°, M.W. 258·4), whereas fractions S₄ and S₅ gave mixtures of palmitic and stearic acids (m.p., 54-55°, M.W. 271·9 and m.p. 53-54°, M.W. 275·9). As the melting points and the mean molecular weights of these two fractions were nearly approaching those of an eutectic mixture (m.p. 54-55°, M.W. 270) of palmitic and stearic acids, it was difficult to separate these acids for identification. Their presence

* This is due to the polymerisation of the small amount of unsaturated acid esters (Iodine value of saturated acid ester, 2·3) at elevated temperature of distillation.

was, however, assumed on account of the finding of palmitic acid in fraction S_3 and stearic acid in fraction S_6 .

The acids from fraction S_6 on crystallisation gave a product melting at $66-67^\circ$ (M.W. 289.8). Its mixed melting point with pure stearic acid was $65-66^\circ$. The product obtained from mother-liquor melted at $63-65^\circ$ (M.W. 299.3). This showed the crystallised acid to be almost pure stearic acid and that the small amount of the higher fatty acid (arachidic acid which has been isolated and identified from the residual esters) present in the fraction got relatively concentrated in the mother-liquor product thereby increasing its M.W. and lowering its m.p.

The acids from the residual esters were dark in colour, soluble in alcohol but only partially soluble in acetone and petroleum ether. They were, therefore, thoroughly extracted with petroleum ether which separated the fatty acids from the resinous matter. The petroleum ether extract on distillation of the solvent was twice crystallised from acetone when minute needles, melting at $76-77^\circ$ (M.W. 308.2), were obtained. The acid is apparently arachidic but on account of the absence of a pure sample of the acid and of insufficiency of the material further identification was not possible. The acids obtained from the acetone mother-liquor had the mean M.W. 291 and were evidently mixtures of arachidic and stearic acids.

Solid Acids (S).

These acids were liberated from the lead salts crystallising out from the lead salts of liquid acids on standing after their separation by Twitchell's method. They melted at 36° and had the mean M.W. of 213.6. Recrystallised from dilute acetone they melted at $40-41^\circ$ (M.W. 204). Mixed melting point with pure lauric acid remained unchanged indicating the portion to be lauric acid. The acids, therefore, contain mainly lauric acid mixed with a small amount of liquid acids.

Liquid Acids (L).

Oxidation.—The liquid acids were saponified to break up any ethyl esters which might have been formed during Twitchell's separation. A portion of the de-esterified acids was converted into potassium soap and oxidised in cold alkaline solution with dilute potassium permanganate according to the modified method of Hazura (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", 6th Ed., Vol. I, p. 575). From the precipitated oxidised acids dihydroxystearic acid, m.p. $131-32^\circ$, M.W. 316.2 and a tetrahydroxystearic acid, m.p. $156-58^\circ$, M.W. 349, were isolated. The filtrate yielded azeleic acid, m.p. $101-02^\circ$, M.W. 186. No hexahydroxystearic acid was found indicating thereby the absence of linolenic acid.

Bromination—Freshly * prepared mixed fatty acids (2.1102 g.), from which unsaponifiable matter was removed, were brominated according to the method of Eibner and Muggenthaler (Lewkowitsch, *loc. cit.*, p. 585) yielding 3.7230 g. of the brominated product but no hexa or higher bromides. Crystallised from petroleum ether the brominated product gave white needles of tetrabromostearic acid (m.p. 113-14°, M. W. 598), the mixed melting point of which with a pure sample of tetrabromo stearic acid remained unaltered. The oxidation and the bromination results thus clearly showed that the liquid acids consisted only of oleic and linoleic acids.

The above data on calculation gave the percentages of the constituent acids as follows:—Lauric (0.6%), palmitic (7.2%), stearic (6.6%), arachidic (1.1%), oleic (35.0%) and linoleic (49.5%).

Unsaponifiable Matter.

The unsaponifiable matter obtained from the sodium soaps of the mixed acids by extraction with ethyl ether, when crystallised from cold alcohol, gave a product melting at 65-66°. This when recrystallised from alcohol melted at 66°-67°. It was not soluble in cold concentrated sulphuric acid, nor was it coloured by the contact of that acid indicating thereby that it was a hydrocarbon. The amount of the hydrocarbon being very small its further identification was not possible.

The mother-liquor from above was concentrated and allowed to crystallise in cold when a product, m.p. 124-25°, separated out. On recrystallisation from alcohol (95%) it melted at 131-32° and its acetyl derivative at 120-21°. The product gave the usual tests for sterols and, therefore, appears to be a mixture of two or more phytosterols at least one of which is the common one, sitosterol, found in vegetable oils.

Carpesterol.

After standing for some days a white flocculent matter, partly suspended and partly settled down, was found in the oil. This was filtered off and crystallised from 95% alcohol forming star-shaped aggregates, m.p. 242-43°.

The substance is insoluble in acid and in alkali and its elementary analysis shows absence of nitrogen and sulphur. It is not affected by boiling with alcoholic potassium hydroxide. Its alcoholic solution does not develop any colour with ferric chloride. It dissolves in concentrated sulphuric acid with a yellow colour which on standing turns deep orange and gives the other characteristic colour reactions of a sterol. The substance, therefore, appears to be a sterol.

* Liquid acids at this stage were found to have undergone polymerisation and were, therefore, not taken for bromination study.

The acetyl derivative of the above substance was prepared in the usual manner and crystallised from alcohol, when needles, m.p. 192° , were obtained. The substance, therefore, appears to be the β -sterol, carpesterol (m.p. 248° ; acetyl derivative, m.p. 194°) isolated by Saiyed and Kanga (*Proc. Indian Acad. Sci.*, 1936, **4A**, 255) and by Gupta and Dutt (*J. Indian. Chem. Soc.*, 1938, **15**, 95), from the fatty oil of the seeds of *S. xanthocarpum*, Schrad and Wendle.

DISCUSSION.

Although there is a fair amount of agreement between the characteristics and the constituents of the fatty oils of the seeds of *S. xanthocarpum* and *S. indicum*, yet a few points of difference may be pointed out. Whereas there is no other satisfactory explanation to offer for the divergence in rotation, specific gravity and unsaponifiable matter content, except the possible inherent physiological difference in the two species, the strikingly high acid value of the *S. xanthocarpum* oil, the high mean molecular weight of its mixed acids (322.7) and the difference in their oleic (42.93%) and linoleic (36.18%) acid percentages may be regarded as due to the polymerised and oxidised state of the oil used in their investigation by Gupta and Dutt. This fact, we think, is sufficiently proved by the comparison of the iodine value of the mixed acids (121.37) as reported by these workers and as computed (103.76) by us from their figures for percentages of the constituent acids.

The characteristics of the fatty oil of another allied *Indica* spp., *S. nigrum*, reported by Pendse (*loc. cit.*) show that the nature of this oil is appreciably different from that of *S. xanthocarpum* and *S. indicum* oils. All these three oils may, however, be put in the semi-drying class occupying places nearer to the drying than to the non-drying limits.

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Received February 27, 1941.

PERIODATES OF QUADRIVALENT METALS.

BY PRODOSH CHANDRA RAYCHODDHURY.

Periodates of a few quadrivalent metals have been prepared and their percentage composition determined.

Little work on the periodates of quadrivalent metals has been done. Cleve (*Bull. soc. chim.*, 1875, ii, 21, 115) has mentioned that periodic acid yields in the solution of a thorium salt, a bulky amorphous precipitate of variable composition. No other periodate of tetravalent metal has been described.

The present investigation was, therefore, undertaken with a view to preparing the periodates of certain tetravalent metals and studying their properties.

EXPERIMENTAL.

Ceric Paraperiodate.—Pure ceric ammonium nitrate was dissolved in dilute nitric acid and on adding to it trisodium paraperiodate ($\text{Na}_3\text{H}_2\text{IO}_6$), dissolved in dilute nitric acid, a shining yellow precipitate was obtained. It was filtered, washed with dilute nitric acid and finally with water and dried in a vacuum desiccator over concentrated sulphuric acid and solid caustic soda. The dry salt formed shining yellow crystals. It liberated iodine when strongly heated. Iodine was estimated volumetrically and cerium as ceric oxide (Found : I, 33.25 ; Ce 36.33. CeHIO_6 , H_2O requires I, 33.22 ; Ce, 36.67 per cent)

Thorium Paraperiodate.—sodium paraperiodate, dissolved in dilute nitric acid, was added in excess to pure thorium nitrate, dissolved in dilute nitric acid. There was no immediate precipitation. The mixture was placed on the water-bath. A white gelatinous precipitate separated after a long time. When the precipitation was complete, it was filtered, washed with dilute nitric acid and finally with water, and dried in a vacuum desiccator. It formed transparent crystals insoluble in water and decomposed on heating to 600° . (Found : I, 24.08 ; Th, 41.9. ThHIO_6 , $5\text{H}_2\text{O}$ requires I, 23.27 ; Th, 42.51 per cent).

Titanium Periodate.—Ammonium titanifluoride was heated strongly in a basin with excess of concentrated sulphuric acid, digested with water for a long time and filtered. Excess of ammonium hydroxide was added to the filtrate, when white gelatinous titanium hydroxide, $\text{Ti}(\text{OH})_4$, was precipitated. It was filtered and washed free of ammonia. Titanium

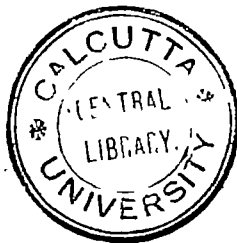
hydroxide was dissolved in dilute nitric acid and added to a solution of $\text{Na}_3\text{H}_2\text{IO}_6$ in dilute nitric acid. At first there was no precipitate. The liquid was concentrated on the water-bath, when a white powdery precipitate was obtained. It was filtered, washed with dilute nitric acid and then with water. It formed opaque crystals. (Found : I, 28'31 ; Ti, 35'65. $7\text{TiO}_2, \text{I}_2\text{O}_7$ requires I, 27'45 ; Ti, 35'20 per cent).

Stannic Periodate.—Stannic chloride was poured into a large excess of ammonium hydroxide, when the white precipitate of stannic hydroxide was precipitated. It was filtered, washed free of chloride, dissolved in dilute nitric acid and added to a nitric acid solution of trisodium paraperiodate. At first there was no precipitate but after a few minutes there was a slight turbidity. On heating it on the water-bath for about fifteen minutes copious white precipitate was formed. It was filtered, washed with dilute nitric acid and then with water and dried over concentrated sulphuric acid in a vacuum desiccator. It formed opaque crystals. (Found : I, 28'19 ; Sn, 49'64 $4\text{SnO}_2, \text{I}_2\text{O}_7$ requires I, 26'6 ; Sn, 49'0 per cent).

Zirconium Periodate.—Zirconium oxide was heated strongly with concentrated sulphuric acid for a long time. The mass was digested with water and filtered. The zirconium sulphate, in the filtrate was treated with excess of ammonium hydroxide, when a white gelatinous precipitate of zirconium hydroxide was precipitated, which was dissolved in dilute nitric acid and added to a solution of $\text{Na}_3\text{H}_2\text{IO}_6$ in dilute nitric acid when immediate white precipitate was formed ; it was kept on the water-bath for a long time for complete precipitation. It was filtered through a Bucher funnel, washed with dilute nitric acid and finally with water and dried in a vacuum desiccator over concentrated sulphuric acid and solid caustic soda. (Found : I, 26'1 ; Zr, 24'6. $3\text{ZrO}_2, \text{I}_2\text{O}_7, 17\text{H}_2\text{O}$ requires I, 24'4 ; Zr, 26'2 per cent).

All the compounds are quite stable and are not affected by boiling water. When strongly heated they all decompose with the liberation of iodine and oxygen.

Work on trivalent, pentavalent and other tetravalent metals are in progress. The author's sincere thanks are due to Prof. P. Rây for kindly suggesting this piece of work and for all the facilities in his laboratory.



STUDIES IN HYDROGEN BOND FORMATION. PART I. AMIDES.

BY A. L. SUNDARA RAO.

The Raman spectra of formamide, acetamide and urea were studied in solutions of water and at increased temperatures. From the changes observed in the $C=O$ frequencies, it is concluded that the amides, particularly formamide and acetamide, are highly polymerised at the laboratory temperatures, and that they break up into lower polymers at higher temperatures as well as in solutions in polar solvents like water.

Latimer and Rodebush (*J. Amer. Chem. Soc.*, 1920, **42**, 1419) proposed that association between molecules takes place through a hydrogen or a proton bond, the conditions for the formation of which are (i) a lone pair of electrons on an atom to act as donor; (ii) hydrogen on molecule from which it is easily removed as hydrogen ion.

Evidence of association has generally been obtained from measurements of heats of mixing, of viscosity, of dielectric constant and of freezing points. But with the developments of new physical methods of studying the structure of molecules, the problem of association has been studied by X-ray diffraction, electron diffraction, infra-red absorption and Raman effect.

The study of the nature of solution by the application of Raman effect has been the subject of a series of investigations by Ramakrishna Rao and collaborators (*Proc. K. Akad. wetensch. Amsterdam*, 1930, **33**, 638; *Indian J. Phys.*, 1937, **11**, 143). Rao (*Proc. Roy. Soc.*, 1931, **A 130**, 489; 1934, **A145**, 489) was the first to use this method for the elucidation of the constitution of water and on the basis of the observed changes in the structure of the Raman band for water with temperature, he postulated the existence of different types of polymers of H_2O molecule. This has been extended by Rao and Koteswaram (*Indian J. Phys.* 1938, **12**, 63) to the study of association in heavy water and by Koteswaram (*Z. Physik*, 1938, **110**, 118; 1939, **113**, 395) to the lower members of the fatty acids.

In the course of a general investigation on molecular association, the author has studied some of the amides and the present paper reports the results of work on formamide, acetamide and urea.

The high boiling points and dielectric constants of the amides have long been recognised as evidence for a high degree of association. Kumler (*J. Amer. Chem. Soc.*, 1935, **57**, 600) has pointed out that this evidence as well as that of cryoscopic data point to a marked difference

in the behaviour of the amides when the hydrogens attached to the nitrogen are replaced by alkyl groups. This evidence points to hydrogen bonding as the mechanism by which association takes place. Smith (*J. Chem. Soc.*, 1931, 2, 3257) and Sugden (*ibid.*, 1924, 125, 1177) measured the parachor values of certain amides at different temperatures and found that they increased steadily with rise of temperature. A drift of this nature was explained as due to the presence of associated molecules at the lower temperature. Coply, Zellhoefer and Marvel (*J. Amer. Chem. Soc.*, 1938, 60, 2666) from the extremely low solubility of monofluorodichloromethane in formamide and acetamide, have suggested the formation of large polymers. Buswell and Rodebush (*ibid.*, 1938, 60, 2444) from the infra-red study of the amides come to the conclusion that amides show a strong tendency towards association. More recently, Saxena (*Proc. Indian Acad. Sci.*, 1940, 11A, 53) studied the association in formamide by the use of Raman effect.

With a view to studying the association characteristics of the amides, the author has studied the effect of temperature and of dilution with water.

EXPERIMENTAL.

The experimental arrangement for exciting the Raman spectra was essentially the same as that proposed by Wood, (*Phil. Mag.*, 1928, 6, 729). The light from the Hg-arc was condensed by a 9" glass condenser on to the Wood's tube containing the solution to be investigated. A combination of two filters consisting of a solution of sodium nitrite and a solution of the proper strength of iodine in carbon tetrachloride was chosen and placed between the condenser and the scattering medium. This served to eliminate the 4047 line of the arc and beyond on the shorter wave-length region, and also the continuous spectrum between 4358 Å and 4916 Å, present in the light from the mercury arc. Care was taken to run the arc at a low voltage, which helps to reduce the continuum considerably. Thus the exciting source is the 4358 line of the mercury arc which is undoubtedly the best mercury line and the Raman lines appear between 4358 and 4916 Å, a region free of mercury lines.

The scattered light was focussed on the slit of the spectrograph by means of an achromatic lens. A two-prism spectrograph of high light-gathering power was used to record the Raman spectrum on Ilford Isochrome plates. A comparison spectrum of copper was given on the same plate using a Hartmann's diaphragm and the wave-length measured

on a Hilger comparator. For such of the lines, which are broad and diffuse, the location of the maximum with the comparator not being possible, a microphotometric record of the entire Raman spectrum was taken. From this record it was easy to find both the position of such lines and their quality in respect of width and diffuseness.

For work at higher temperatures, the Wood's tube, containing the substance to be investigated, was placed inside a cylindrical electrical heater of 5 cm. in diameter and 28 cm. long, open at either end. The heater was provided on one side with a window of 2×14 cm. for allowing the incident radiation. By this arrangement the temperature could be kept within a range of $\pm 0.5^\circ$.

Purification of Solutions.

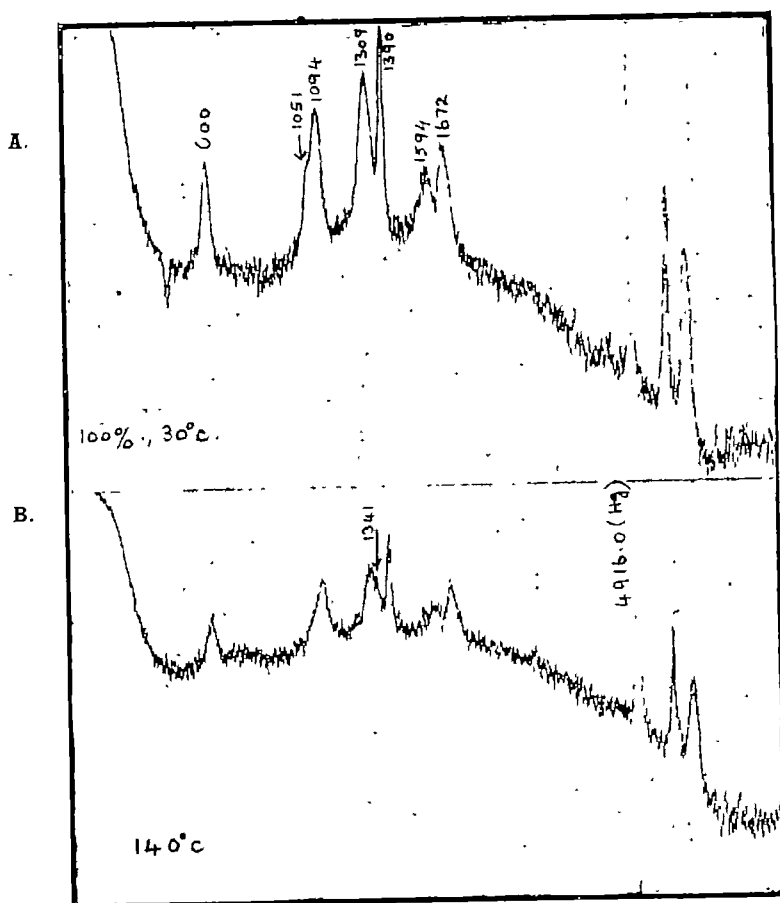
All the amides investigated show a very strong continuous background masking to a great extent the Raman lines. Merck's bidistilled formamide, when kept for exposure showed a strong continuous spectrum in the region 4046\AA — 4916\AA and beyond to the green line of the mercury arc. So, the liquid was further purified by distilling it twice at low pressure and at 110° . The sample thus obtained was found to be free to a large extent from the continuum and was used throughout the course of these investigations.

In the case of solutions of acetamide and urea, the method previously adopted by the author for purification of sugar (*Indian J. Phys.*, 1940, **14**, 207) was found to be successful. It consists in shaking the solution with Norit A (the carbon used being about 3% of the weight of the amide in the solution) and then heated for 15 to 20 minutes at 70° with stirring. The solution was then filtered through a sintered glass funnel in which a filter paper of fine pore was put. The filtrate was collected and poured on to the filter repeatedly 5 or 6 times, thus removing the dust particles from the filter system. The filtrate was then allowed to flow directly into the Wood's tube. The solutions thus prepared were remarkably clear and gave spectra entirely free from continuum. Control experiments with Norit A in distilled water were done in order to make sure that there were no Raman lines or bands not found in pure water. The remarkable property of the decolorising carbon on the removal of continuum could be explained on the well known property of carbons to adsorb impurities, and it might be that the fluorescent impurities, which are responsible for the continuous spectrum, were removed during the above method of purification. Double distilled conductivity water was always used in the study of the amides at different dilutions.

Formamide.

The Raman spectrum of this substance has been previously studied by Kohlrausch and Pongratz (*Z. physikal. Chem.*, 1934, **B27**, 176,) and more recently by Saxena (*loc. cit.*). This could be obtained in 15 hours by the author. The effect of water on formamide was studied at 75%, 50% and 25% concentration of formamide, and proportionately increased exposures were given for the different dilutions. The effect of solution in some of the non-polar solvents like benzene, ether, etc. could not be

FIG. 1.
Formamide.



studied owing to the general insolubility of all the amides investigated in these solvents. Formamide was investigated at 30° and at 140°. Figs. 1 (A and B) contains the microphotometric curves of the Raman spectra

of formamide taken under different conditions. Table I gives the Raman frequencies of this substance. The figures in parenthesis indicate the relative visual estimates of the intensities. For the sake of brevity, the assignment of the various frequencies are given in column IV of the table. In columns I and II are given the results of the previous investigators for purposes of comparison.

TABLE I.

Formamide.

Kohlrausch and Pongratz (1934)	Saxena (1940)	Author.	Assignment.
	200 (3) br	201 (3) V. br	
608 (4)	603 (4)	600 (4)	
	700 (o)		
	780 (o)		
1005 ($\frac{1}{2}$)			
1050 (1)	1048 (o)	1051 (1)	C—N
1094 (2) br	1095 (2) br	1094 (3) br	
1314 (6)	1305 (5) V. br	1309 (5) br	
		1341 (1, s)	
1390 (10) s	1391 (10) s	1390 (10) s	
1599 ($\frac{1}{2}$)	1591 (1)	1594 (2)	C=O
1672 \pm 11 (2)	1672 (2)	1673 (3)	
	2008 (o)		
	2083 (1)		
	2695 (o)		
	2766 (1)		
2882 (8) br	2885 (8) br	2884 (8)	Valence C—H
	3176 (4)	3183	N—H
	3265 (1)	3215	
3347 (1)	3338 (2)	3298	
3376 (1)	3480		

The intensity and frequency changes of the various Raman lines of formamide under the different conditions studied are discussed in brief below.

(i) $\Delta\nu=600$. With dilution in water it diminishes in intensity and becomes broad and diffuse at 25% dilution. Similar changes are observed with increase of temperature from 30° to 140°

(ii) $\Delta\nu=1051$. This is the faint component accompanying the 1094 line and disappears at higher temperatures.

(iii) $\Delta\nu=1341$. This is a weak line which is not present at the laboratory temperature but appears at the higher temperature. A similar effect was not noticed in dilutions with water, probably due to the increased continuum in solutions.

(iv) $\Delta\nu=1390$. The sharp line at 1390 shows a shift of 6 cm^{-1} at 25% dilution. A similar change was observed with increase of temperature.

(v) $\Delta\nu=1594, 1672$. These are the C=O frequencies. At the higher temperature the intensity of the 1594 line is considerably decreased. The line 1672 is broad with the sharp edge towards the 4358\AA line of the mercury arc, and has an intensity maximum at the edge. At the higher temperature, this maximum shifts to longer wave-length and there is a shift of about 8 cm^{-1} . The effect of dilution has a similar change on the Raman spectrum of this substance in this region.

(vi) $\Delta\nu=2884$. This is the C—H frequency and indicates no change either in solutions or with temperature changes.

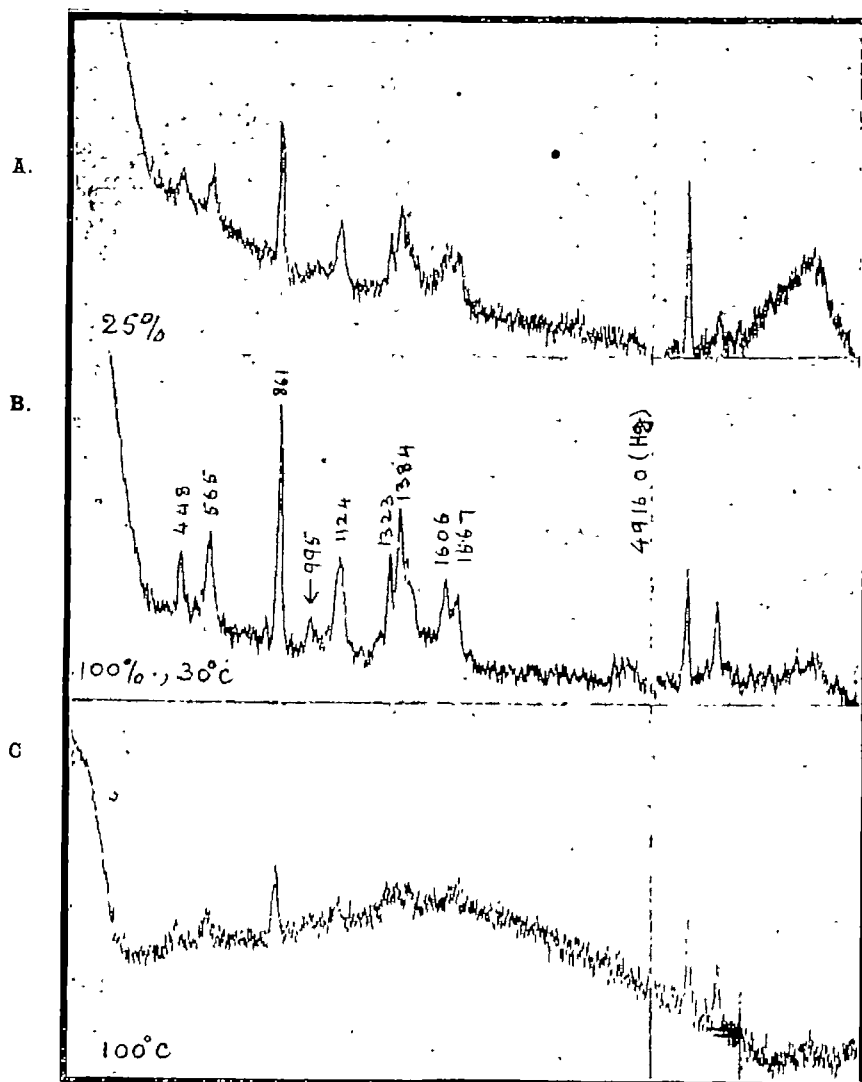
Acetamide.

The Raman spectrum of this substance has previously been studied by Kohlarusch and Pongratz (*loc. cit.*) in the molten state and by Ananthakrishnan (*Proc. Indian Acad. Sci.*, 1937, **5A**, 200) in the crystal state. As far as the author is aware, there is no work reported on this substance in solutions of water. The Raman spectrum of this substance was obtained in 10 hours. The microphotometric curves of the Raman spectra taken under different conditions are given in Fig. 2 (A—C). Table II gives the Raman frequencies of acetamide along with those reported by the previous investigators. The assignment of the frequencies to the respective valence bonds are given in column 4 of the table. The intensity and frequency changes of the various Raman lines of acetamide under the different conditions studied are discussed in brief below.

(i) $\Delta\nu=448, 565$. These are the low frequency lines ascribed to the external oscillation in the molecule. The intensity of these lines falls off and they become diffuse as dilution progresses. A similar change is observed with increase of temperature

(ii) $\Delta\nu=861, 995$. Of these 861 is the C—C frequency. The 861 line diminishes considerably in intensity with dilution and change of temperature and slightly increases in its frequency, the shift being about 4 cm^{-1} . The

Fig 2.
Acetamide.



weak line at 995, which is ascribed to C—N, disappears at higher dilutions and temperature.

(iii) $\Delta\nu=1124$. It falls off in intensity and becomes diffuse at higher temperatures and changes in frequency by 10 cm^{-1} .

(iv) $\Delta\nu=1323, 1384$. 1323 is a sharp line and tends to disappear at higher dilutions. With increase of temperature the effect is more pronounced. 1384 is a broad line with its intensity maximum towards the exciting line. With increase of temperature and in solutions the line shifts to a higher Raman frequency, the shift being 6 cm^{-1} .

(v) $\Delta\nu=1606, 1667$. There are C=O frequencies. With dilutions in water, 1606 line diminishes in intensity and shifts to 1610 . The 1667 line remains very nearly unchanged in dilute solutions. But with increase of temperature more marked changes were observed; the lower frequency disappears altogether and merges into a broad band with intensity maximum at 1673 .

(vi) $\Delta\nu=2930, 2965$. There are the C-H frequencies. Of these 2930 is the stronger line. They remain unchanged both in solutions in water and at increased temperatures.

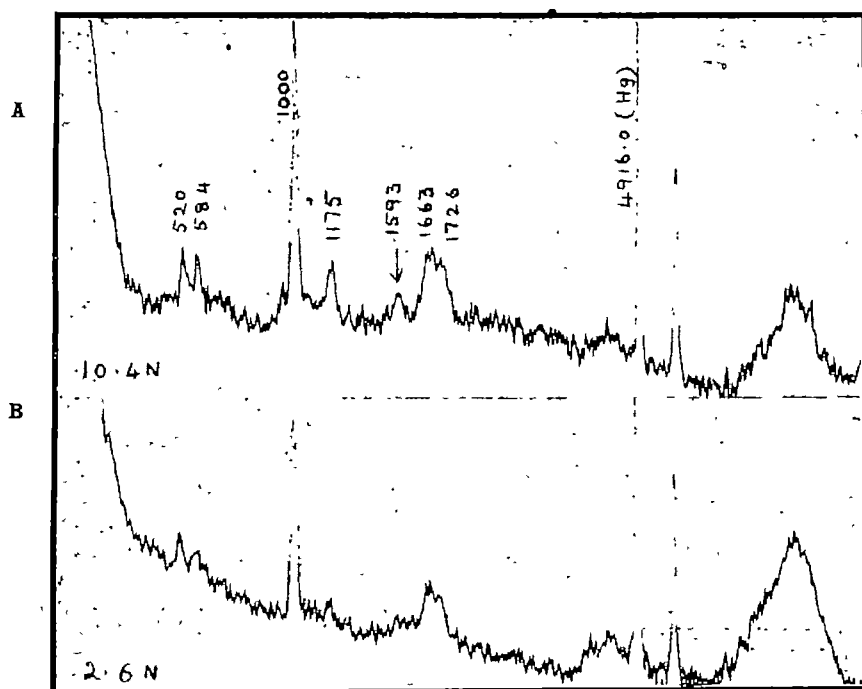
TABLE II.

Kohlrausch and Pongratz (molten).	Ananthakrishnan. (crystal)	Author. (aq. soln.).	Assignment.
236 (o)			
448 (3)	455 (1) S	448 (3)	
564 (3)		565 (4)	
862 (7) br	875 (8) S	861 (8) S	C—C
		995 (1)	} C—N
1119 (3) br	1147 (5) S	1124 (3) br	
1344 (3) br	1354 (3)	1323 (3) br	
1387 (3) br	1397 (3) diff.	1384 (4) br	
1422 (3)			
1611 (2)	1594 (1) diff.	1606 (2) br	} C=O
1660 \pm 9 (3) br		1667 (2) br	
2933 (6) br	2933 (10) S	2930 (5)	} valence C—H
2958 (2)	2970 (o) d	2965 (1)	
	3020 (o) d		
	3150 (6) br		
	3286 (1) diff		
	3351 (4) diff.		

Urea.

The Raman spectrum of this substance has previously been studied by Kohlrausch and Pongratz (*loc. cit.*) and Edsall (*J. Chem. Phys.*, 1935 **4**, 1) in aqueous solution, and Ananthakrishnan (*loc. cit.*) in the crystal state. The Raman spectrum of this substance could be obtained in 20 hours. The microphotometric curves of the spectra taken under different conditions are given in Fig. 3 (**A** and **B**). No marked changes either in intensity

Fig 3.

Urea.

or frequency were observed with urea in solutions with water.

(i) $\Delta\nu=520, 584$. Except for decrease in intensity, the lines remain unchanged.

(ii) $\Delta\nu=1175$. It becomes sharper with dilution and finally tends to disappear.

(iii) $\Delta\nu=1593, 1663, 1726$. These are the C=O frequencies. Of these the 1593 only disappears at higher dilutions. The other two lines 1663, and 1726 remained unchanged in their frequency and in their outward appearance.

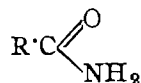
Table III gives the frequencies of urea along with those reported by other observers.

TABLE III.

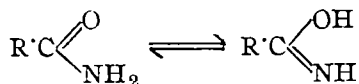
Edsall (aq. solution.).	Ananthakrishnan (crystal).	Author (aq. solution).	
541 (1)		520 (2)	
584 (1)		584 (1)	
1000 (6)	1012 (10) S	1000 (10) S	} C-N
1170 (1) V. br	1171 (1) diff.	1175 (2) br	
1468 (0)	1465		
1580 (0)	1537 (2)	1593 (1)	} C=O
1666 (1) b	1576 (1)	1663 (2) br	
1768 (7)		1726 (1) br	
3230 (1)	3243 (2) diff.		
	3334 (4) diff.		
3380 (3) br	3353 (5) diff.		
3489 (1) br	3434 (5)		

DISCUSSION.

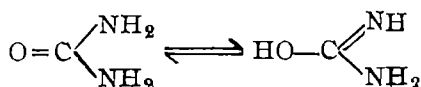
The classical structure assigned to the unsubstituted amides is



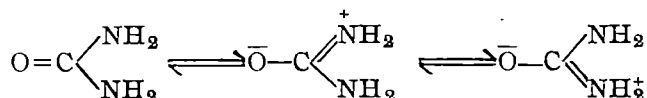
But certain reactions of the amides, such as alkylation, indicate that they may have the alternative tautomeric structures as



Kohlrausch and Pongratz (*loc. cit.*) ascribe the two frequencies in acetamide, $\Delta\nu = 1611, 1660$ observed in the C=O region as due to the tautomeric modifications as suggested above. Krishnamurty (*Indian J. Phys.*, 1931, 6, 309) suggests a similar tautomeric arrangement in the case of urea as:

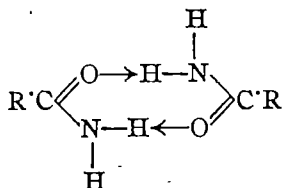


and Pauling ("Nature of Chemical Bond", 1939) has suggested

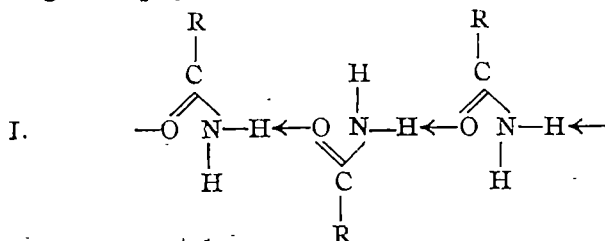


But as is shown later in the discussion, it is not possible to have a great proportion of the tautomer molecules. This is supported by the dipole moment measurements of Kumler and Porter (*J. Amer. Chem. Soc.*, 1934, **56**, 2549).

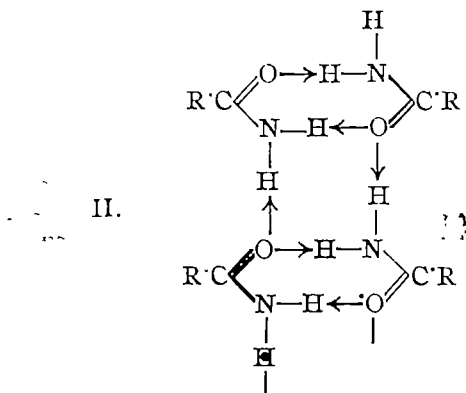
From the changes observed with dilution and temperature, it can be said that the acid amides, formamide and acetamide, show a greater tendency towards association. It is not possible to deduce with certainty whether the intramolecular association is the result of $\text{NH} \leftarrow \text{N}$ or $\text{NH} \leftarrow \text{O}$ bonding, and as the $\text{O} \rightarrow \text{H}$ bonding is much stronger than the $\text{N} \rightarrow \text{H}$ bonding, it could be expected that the former type of bonding would exist in associated amides. The work of Rodebush and Buswell (*loc.cit.* also *J. Amer. Chem. Soc.*, 1939, **61**, 3252) on glycylglycine ethyl ester, and some of the monosubstituted amides show definitely a strong infra-red absorption a little beyond 3.0μ indicating bonded $\text{O}-\text{H}$ rather than $\text{N}-\text{H}$. So, the associated molecule in an amide could be represented as



In such a postulated molecule, the hydrogens occur not involved in bond formation, attached directly to the ring of the double molecule, and these additional hydrogens might interfere with the formation of stable dimers. We have an analogy in the case of formic acid, where in the pure acid, the dimers give way to polymers, because of the bonding action of the hydrogen attached to the carbon. Thus, in the case of unsubstituted amides, it can be said that the association proceeds to a higher stage and forms large sized polymers as



or by the "fusing" of dimers as



But the formation of a polymer as represented in the second type requires sharing of the second pair of electrons on the oxygens. So, it could be said that the amides exist as linear polymers as shown in type I.

Of course, in the case of monosubstituted amides, the hydrogen is replaced by R and the existence of dimers in these amides has been shown by Rodebush and Buswell (*loc. cit.*) and they also suggest that enolisation can take place only in associated molecules.

In the case of solutions of formamide and acetamide in water, we have an associated solute in solution in another associated solvent, and it is well known that in such a system there will be the tendency for mutual dissociation. Thus, any change caused by association or dissociation of the molecules must affect the frequencies of the C=O group most, as they are nearest to the hydrogen bond.

The CH₃ and C—C linkages are not affected to such a large extent. With the formation of a hydrogen bond, the C=O binding weakens, thus giving rise to a diminished frequency. While, with the breaking up of such a bond the opposite effect takes place, resulting in a strengthening of the binding and a consequent increase in frequency.

The changes observed in formamide and acetamide, definitely indicate that there is dissociation of the more complex molecules into simpler ones as is evidenced in formamide by the shift of the C=O frequency 1672 to 1680 cm.⁻¹ The 1594 line almost disappears at the higher temperature, and at 25% dilution. So, the lower frequency seems to be characteristic of the associated molecules. Similar changes in the carbonyl frequency were also noticed in acetamide. Koteswaram (*loc. cit.*) observed analogous changes in the carbonyl frequency of the carboxyl group in formic and acetic acids. The 600 line in formamide, and the 565 line in acetamide,

could be ascribed to an external oscillation in the molecule. The increased diffuseness of this line with dilution or with increase of temperature indicates that there may be the superposition of two lines—one corresponding to the associated molecules at the lower temperature, and the other due to the depolymerised molecules in solution or at higher temperatures. Similar changes were also observed in the author's work on glycerine (*Indian J. Phys.*, 1940, **4**, 365).

The feeble component lines 1051 in formamide and 995 in acetamide may be due to the C-N oscillations of the associated molecules and therefore naturally disappear at the higher temperatures and dilutions as the molecules giving rise to these lines are depolymerised. Thus, it would be seen from the foregoing results that the molecular complexity of the amides decreases with increase of temperature or with dilution. Similar conclusions were arrived at by Turner (*J. Chem. Soc.*, 1910, **97**, 2069) by the measurement of association factors at different temperatures, and by Smith (*loc. cit.*) from measurements of the parachor value between 18° and 50°.

The author desires to express his very grateful thanks to Dr. I. Ramakrishna Rao for his helpful guidance and interest throughout the progress of this investigation.

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Received March 7, 1941.

MAGNETISM AND CATALYSIS. PART III. CHLORINATION OF CHLOROFORM TO CARBON TETRACHLORIDE IN PRESENCE OF FERRIC CHLORIDE.

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ANAND SWAROOP BHATNAGAR.

The rôle of ferric chloride as an inhibitor in the chlorination of chloroform to carbon tetrachloride has been studied with the help of the magnetic method. The inhibitory action has been observed to be absent if the sample of chloroform be completely free from moisture which in itself has a catalytic effect upon the reaction. The action of ferric chloride has been explained as an outcome of the presence of moisture with which ferric chloride forms a hydrated complex which acts as an inhibitor in this case.

It is well known that if proper precautions are not taken, methane on chlorination yields a number of chloro derivatives which are formed as the result of successive replacement of hydrogen by chlorine in methane. If, however, chloroform alone be chlorinated then carbon tetrachloride is formed. The chlorination of the hydrocarbon is influenced by (i) light, (ii) temperature, and (iii) catalysts. Bedford and collaborators (*Ind. Eng. Chem.*, 1916, 8, 1029, 1091) investigated the influence of light on the chlorination of methane and concluded that a large share of the actinic power of the quartz lamp lies in the ultraviolet rays but that is not required for chlorination process.

Blanc (U. S. P., 1248065, 1917) used light as well as catalysts for the chlorination of saturated hydrocarbons. Gault and Truffault (*Compt. rend.*, 1924, 179, 467) from chlorination of chloroform to carbon tetrachloride observed that the reaction did not take place in the dark and was not influenced up to a wave-length $\lambda=639$; but the reaction commenced in the violet region and was very vigorous in the beginning of the ultraviolet region. The reaction becomes feeble below $\lambda=400$. According to Gault and Truffault (*loc. cit.*) the reaction does not take place at very low temperatures but it commences towards -5° and becomes vigorous between 5° and 10° . Iron perchloride, when used as a catalyst, was found by them to behave as an inhibitor, whereas catalysts like calcium chloride were found to have no influence on the reaction. In explaining the part played by ferric chloride as an inhibitor, they suggested that ferric chloride did not take part in the

reaction, but it simply helped in the absorption of particular wave-lengths of light which determined the chlorination at that temperature. If that be so, then the magnetic property of the chlorinated solution will obey the mixture law, but if ferric chloride takes part in the reaction and a new compound is formed, then its formation in the intermediate stages, even though it may not be revealed by ordinary methods of analysis, would be shown by the magnetic analysis of the chlorinated solution.

The main object of the present investigation is, therefore, to ascertain the rôle of ferric chloride as an inhibitor in this reaction with the help of the magnetic method.

EXPERIMENTAL.

The susceptibility values were determined on a modified form of Guoy's balance (*vide supra*). In case of solutions, susceptibility has been calculated with the help of the relation :

$$\chi_{\text{soln}} = \chi_{\text{salt}} \times C_{\text{salt}} + \chi_{\text{solvent}} \times (1 - C_{\text{salt}})$$

The following values of susceptibilities were obtained for the various reagents.

TABLE I.

Reagents.	χ .
Chloroform	-0.517×10^{-6}
Carbon tetrachloride	-0.422
Ferric chloride (solid)	$+82.05$
Ferric hydroxide (solid)	$+157.0$

TABLE II.

Constants.	Prepared sample.	Literature.
χ	-0.545×10^{-6}	$-(0.488-0.588)10^{-6}$
Density	1.5035	1.5264
Refrac. index	1.4429	1.4462
B. P.	64.3°	61.2°.

Pure anhydrous ferric chloride was prepared by passing a stream of dry chlorine over iron filings at a temperature of 800°-900°. The small amounts of ferric chloride used as catalyst could not be determined by ordinary gravimetric or volumetric methods, therefore the quantities were estimated colorimetrically by using 7-iodo-8-hydroxyquinoline-5-sulphonic acid as an indicator. The results obtained were further checked by using potassium sulphocyanide as an indicator.

Pure chloroform was prepared from a sample available in the stores by firstly shaking the sample with water to remove traces of alcohol which are often associated with chloroform and then distilling it after having kept

it over fused calcium chloride for forty-eight hours. Various physical constants of the sample, thus obtained, were determined and are tabulated in Table II along with the values given in literature.

The divergence between the observed values and those given in literature for various constants may be due to some water, the presence of which is further supported by the colour imparted by this sample of chloroform to anhydrous copper sulphate.

TABLE III.

FeCl ₃ .	Refractive index.	Susceptibility values of		
		CHCl ₃ .	CHCl ₃ + FeCl ₃ .	CHCl ₃ + FeCl ₃ (calc. on mixture law).
0.0165%	1.4436	-0.526×10^{-6}	-0.504×10^{-6}	-0.512×10^{-6}
0.0165	1.4429	-0.549	-0.524	-0.535
0.0208	1.4429	-0.545	-0.512	-0.527
0.0170	1.4425	-0.553	-0.539	-0.542
0.0338	1.4425	-0.554	-0.527	-0.530

It was further observed (Table III) that when the susceptibility values of solutions of ferric chloride in this sample of chloroform were determined, the observed values did not agree with the values calculated on mixture law assuming that ferric chloride or chloroform did not undergo any change. The observed susceptibility values were always lower than the calculated ones indicating thereby that some compound with higher paramagnetic value was being formed.

Ferric chloride readily undergoes hydrolysis to ferric hydroxide in the presence of moisture and ferric hydroxide is more paramagnetic ($+157 \times 10^{-6}$) than ferric chloride ($+82.05 \times 10^{-6}$). It appears, therefore, that the divergence observed between the calculated and observed values of a solution of ferric chloride in chloroform may probably be due to the formation of more paramagnetic ferric hydroxide due to hydrolysis of ferric chloride.

To remove even the last trace of moisture from chloroform the following method was followed. Chloroform, distilled over fused calcium chloride, was kept over phosphorus pentoxide for a couple of days and then it was filtered and distilled. It was not distilled over phosphorus pentoxide, as there was the danger of the formation of a small quantity of carbonyl chloride. The sample, thus prepared, did not give blue colour with anhydrous copper sulphate and the various physical constants determined for this sample agree well with those given in literature.

TABLE IV.

Constants.	Prepared sample.	Literature.
Magnetic susceptibility	0.517×10^{-6}	$(0.488-0.588)10^{-6}$
Density	1.5259	1.5264
Refractive index	1.4444 (at 28°)	1.4462 (at 20°)
Boiling point	61°	61.2°

When magnetic susceptibility of solutions of freshly prepared anhydrous ferric chloride in pure dry chloroform was determined, the observed and the calculated values agreed well (Table V) indicating that the ferric chloride did not undergo any change.

TABLE V.

FeCl ₃ .	Refractive Index.	Susceptibility values of		
		CHCl ₃ .	CHCl ₃ +FeCl ₃ (obs).	CHCl ₃ +FeCl ₃ (calc.).
0.0182%	1.4444	-0.517×10^{-6}	-0.501×10^{-6}	-0.502×10^{-6}
0.0191	1.4444	-0.517	-0.499	-0.500

Chlorination.

Dry chlorine gas was bubbled simultaneously through two wide-mouthed flasks one containing pure chloroform and the other containing chloroform and small amount of ferric chloride. The flasks were kept in a bath maintained at 5°, since at this temperature maximum amount of chlorination took place. The flow of gas in both the flasks was controlled by a flow meter. After chlorination the excess of chlorine dissolved in solutions had to be removed. Gault and Truffault had suggested the use of mercury and arsenious oxide but these reagents on account of their slight solubility in chloroform could not be used. Therefore displacement of dissolved chlorine by an inert gas such as nitrogen was resorted to. Pure nitrogen, free from moisture, as indicated by anhydrous copper sulphate, was bubbled through the flasks till no iodine was liberated on addition of potassium iodide and potassium fluoride. The samples were then kept in vacuum till further use.

After chlorination amount of carbon tetrachloride formed was determined either by measuring the density or the refractive index of the solution. The susceptibilities were determined on a Guoy's balance and the results are tabulated below.

TABLE VIA.

Chlorination of chloroform containing traces of moisture.

Time.	Mixture after chlorination			Amount of	
	Refrac. index of CHCl_3 .	Refrac. index.	Density.	CHCl_3 .	CCl_4 .
3 hrs.	1'4429	1'4450	1'5392	85'71%	14'29%
6	1'4425	1'4502	1'5782	49'00	51'00
12	1'4429	1'4570	1'6260	4 08	95 92

TABLE VIB.

Chlorination of moist chloroform in presence of ferric chloride.

Time.	Amount of			Mixture after chlorination.	
	FeCl_3 .	CHCl_3 .	CCl_4 .	Refrac. index.	Density.
3 hrs	0'0165%	93'87%	6'13%	1'4438	1'5305
6	0'0338	87'41	12'59	1'4444	1'5373
12	0'0208	78 23	21 77	1'4461	1'5471

TABLE VIC.

Susceptibilities.

Time.	Amount of FeCl_3	χ of pure chloroform.		χ of chloroform and ferric chloride.	
		Before chlorination.	After chlorination.	Before chlorination.	After chlorination.
3 hrs.	0 0165%	$-0'549 \times 10^{-6}$	$-0'540 \times 10^{-6}$	$-0'524 \times 10^{-6}$	$-0 516 \times 10^{-6}$
6	0'0338	$-0'554$	$-0'497$	$-0'530$	$-0'522$
12	0'0208	$-0'545$	$-0'443$	$-0'512$	$-0'495$

In all the three samples chlorinated for different times a definite inhibition of chlorination of chloroform by ferric chloride was observed. After 12 hours the chlorination of chloroform was almost complete (95'92%) in the absence of catalyst while in the presence of ferric chloride only

21.77% of chloroform was transformed to carbon tetrachloride. The carbon tetrachloride obtained by fractional distillation of the mixture of chloroform and carbon tetrachloride had $\chi = 0.438 \times 10^{-6}$, refractive index = 1.4576 and density = 1.6304.

Chlorination of completely moisture-free chloroform was also studied (Table VII).

TABLE VIIA.

Chlorination of completely moisture-free chloroform.

Time.	Refractive index of CHCl_3 before chlorination.	Amount of		• Mixture after chlorination.	
		CHCl_3 .	CCl_4 .	Refrac. index.	Density.
3 hrs.	1.4444	90.41%	9.59%	1.4458	1.5359
6	1.4444	74.65	25.35	1.4481	1.5529
12	1.4444	43.83	56.17	1.4526	1.5857

TABLE VII B.

Chlorination of moisture-free chloroform in presence of ferric chloride.

Time.	Amount of FeCl_3	Amount of		Mixture after chlorination.	
		CHCl_3 .	CCl_4 .	Refrac. index.	Density.
3 hrs.	0.0182%	90.41%	9.59%	1.4458	1.5359
6	0.0191	75.34	24.66	1.4481	1.5521
12	0.0191	43.83	56.17	1.4526	1.5857

TABLE VII C.

Susceptibilities.

Time	Amount of FeCl_3	χ of pure chloroform.		χ of chloroform + ferric chloride.	
		Before chlorination.	After chlorination.	Before chlorination.	After chlorination.
3 hrs.	0.0182%	-0.517×10^{-6}	-0.508×10^{-6}	-0.501×10^{-6}	-0.496×10^{-6}
6	0.0191	-0.517	-0.493	-0.500	-0.480
12	0.0191	-0.517	-0.464	-0.500	-0.457

In these cases it is observed that ferric chloride does not act as an inhibitor and the extent of chlorination both in the presence and absence of catalyst is the same.

DISCUSSION.

From the results tabulated in Tables VIA and VIIA it is clear that moisture acts as catalyst in the chlorination of chloroform to carbon tetrachloride. This observation is in accord with the work of Baker and collaborators (*J. Chem. Soc.*, 1886, 47, 349; 1894, 68, 611; 1898, 73, 422; 1925, 127, 1990) who have shown that absence of moisture inhibits many reactions.

Gault and Traffault (*loc.cit.*) in trying to explain the part played by ferric chloride in the reaction under investigation showed that there are certain active radiations that are responsible for the chlorination of chloroform, and the inhibition they ascribed to the absorption of these radiations by ferric chloride. If that were so, the amount of carbon tetrachloride, formed on the chlorination of a sample of pure dry chloroform in the presence of ferric chloride, would have been less than that formed in the absence of ferric chloride, but this is contrary to observations as is clear from Tables VIIA and VIIB.

Results tabulated in Table VI(A—C), however, reveal that chlorination of chloroform containing traces of moisture is retarded in the presence of ferric chloride. Furthermore, the observed susceptibility value of the chlorinated solution does not agree with the susceptibility value calculated according to the mixture law assuming that ferric chloride exists as such in the solution and does not undergo any change.

It may be suggested that a new intermediate compound of ferric chloride with chloroform having susceptibility value different from ferric chloride might have been formed. If that were so, then such a compound ought to have also been formed when pure dry chloroform was chlorinated in presence of ferric chloride and the calculated and observed susceptibility values ought to have been different. But from results given in Table V it is clear that calculated and observed values are in excellent agreement. Hence the possibility of the formation of an intermediate compound of ferric chloride and chloroform from the magnetic data is ruled out.

Ferric chloride may combine with water to form a hydrate or it may react with water in chloroform to form ferric hydroxide and thus the new compound formed may be responsible for the inhibition of the reaction.

Usually the susceptibility value of the hydrates of paramagnetic compounds is less than that of their anhydrous variety. So if FeCl_3 combines with moisture in chloroform and forms a hydrate, which is responsible for inhibition, the observed susceptibility of the solution of ferric chloride in chloroform containing traces of moisture should be more diamagnetic than the calculated value of the solution assuming that ferric chloride in solution exists as such. But from Table III, it is clear that the observed susceptibility value shows the formation of a more paramagnetic compound.

Ferric hydroxide is more paramagnetic than ferric chloride. If susceptibility value of the chlorinated solution of chloroform in the presence of ferric chloride be calculated assuming that whole of ferric chloride is converted to ferric hydroxide, then even the calculated susceptibility value does not agree with the observed value. The observed susceptibility value, however, lies between the susceptibility value calculated on the assumption that whole of ferric chloride exists as such and that calculated on the assumption that the whole of the ferric chloride is converted to ferric hydroxide. It suggests that in chloroform containing traces of moisture, part of the ferric chloride exists as such and part is hydrolysed to ferric hydroxide. The inhibition of this reaction by ferric chloride in presence of moisture, therefore, can be attributed to the formation of ferric hydroxide and not to ferric chloride.

But the fact that passage of dry chlorine for a long time in the solution, which would most probably under the circumstances react with ferric hydroxide and set free ferric chloride and water, does not influence the efficiency of ferric chloride as an inhibitor in the presence of moisture, produces doubt as to the correctness of the formation of ferric hydroxide from ferric chloride.

It seems that ferric chloride combines with water and forms a new complex which is not attacked by chlorine in chloroform and because the complex is more paramagnetic than anhydrous ferric chloride, therefore it is not an ordinary hydrate which would have been less paramagnetic than anhydrous ferric chloride. The inhibition of chlorination of chloroform by ferric chloride, as observed by Gault and Truffault, seems to be due to the fact that their samples of chloroform contained some moisture absorbed which was difficult to detect by ordinary chemical methods and consequently part of the ferric chloride formed the new complex, which was responsible for the observed inhibition.

The rôle of the new complex formed in the reaction can be explained by suggesting that moisture, which, as has been shown to act as a catalyst in the process of chlorination, is removed by ferric chloride and thus the

reaction is inhibited. If that was the only cause then the percentage of carbon tetrachloride formed on chlorination should be either equal to or more than that formed when chloroform containing no moisture is chlorinated, according to whether whole or part of the moisture is removed by ferric chloride.

But actually as it is clear from Tables VI and VII, the percentage of carbon tetrachloride formed by chlorination of pure chloroform is more than that formed on the chlorination of chloroform containing moisture and ferric chloride.

Gault and Truffault, as a result of their investigations attributed inhibition to the absorption of active radiations which favour chlorination of chloroform. It seems, therefore, that besides the removal of the catalyst water by ferric chloride, the absorption of active radiation by the complex which favour chlorination are also responsible for the inhibition of the chlorination of chloroform by ferric chloride as suggested by Gault and Truffault.

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Received March 7, 1941.

THE ACTION OF CHLORINE ON THE HYDROXIDES OF IRON AND CHROMIUM IN THE PRESENCE OF IODINE.

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By passing a brisk current of chlorine through a boiling solution of iodine in iron (ic) hydroxide and chromium hydroxide, $\text{FeIO}_5, 11\text{H}_2\text{O}$ and $\text{Cr}_2\text{O}_3, 2\text{I}_2\text{O}_7, 22\text{H}_2\text{O}$ were obtained respectively.

Bahl and Singh (*J. Indian Chem. Soc.*, 1940, 17, 168, 398) have studied the action of chlorine on the hydroxides of lithium, potassium and alkaline earths. They found that in the case of alkali metal hydroxides, periodates are formed while in the case of alkaline earth hydroxides, iodates are formed. We have taken up the present work on the same lines and have found that in the case of the hydroxides of iron, periodates of the composition, $\text{FeIO}_5, 11\text{H}_2\text{O}$ and of chromium, $\text{Cr}_2\text{O}_3, 2\text{I}_2\text{O}_7, 22\text{H}_2\text{O}$ are formed respectively.

EXPERIMENTAL.

Freshly prepared hydroxides of iron (Fe^{III}) and chromium were taken in suspension in water and powdered iodine was added to it. A brisk current of chlorine was then passed through the hot suspension of iodine in the hydroxides. In the case of ferric hydroxide a light brown precipitate was formed, whereas a clear solution was obtained in the case of chromium hydroxide by the above treatment. On adding alcohol to the clear solution formed in the case of chromium, a green precipitate was obtained. The precipitates were filtered, washed with hot water, and dried at 400° . The green precipitate of chromium was found to be insoluble in water like most of the periodates. Metals were determined as oxides. Iodine and available oxygen were estimated by methods adopted by Partington and Bahl.

TABLE I.

Iron salt.

Sample No.	Iron.		Iodine.		Available oxygen.	
	Found	Calc.	Found.	Calc.	Found.	Calc.
1.	12.04%	12.14%	27.80%	27.54%	12.20%	12.14%
2.	12.04	„	27.70	„	12.40	„
3.	12.00	„	27.75	„	12.20	„

These results correspond to the formula $\text{FeIO}_6, 11\text{H}_2\text{O}$. This salt has also been obtained by the interaction of ferric salt with potassium periodate (Mellor, "A Comprehensive Treatise in Inorganic and Theoretical Chemistry", 1922, Vol. II, p. 416).

TABLE II.
Chromium salt.

Sample No.	Chromium.		Iodine.		Available oxygen.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	8.05%	8.12% •	39.70%	39.69%	17.50%	17.50%
2.	8.20	„	39.89	„	17.40	„
3.	8.35	„	39.83	„	17.50	„

These values correspond to $\text{Cr}_2\text{O}_3, 2\text{I}_2\text{O}_7, 22\text{H}_2\text{O}$. The ratio of iodine to oxygen is 2 to 7.

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Received April 15, 1941.

PHOTOSENSITISATION BY SOLIDS. PART III. PHOTO-SENSITISED OXIDATION OF AMMONIA IN AQUEOUS SOLUTION WITH COLLOIDAL TITANIA AS THE PHOTOSENSITISER.

BY G. GOPALARAO AND CH. I. VARADANAM.

The photosensitised oxidation of ammonia in the total ultraviolet light from the quartz-mercury vapour lamp has been studied using negatively charged colloidal titania as the photosensitiser. The rate of reaction is found to be practically unaffected by temperature and the concentration of ammonia. The decrease of reaction velocity on the addition of suitable flocculating ions shows that the reaction is a heterogeneous one. The mechanism of the reaction has been discussed.

In Part I of this series Gopalarao (*Z. physikal. Chem.*, 1930, **A**, 184, 377) discussed the mechanism of the photosensitisation by titania by studying the simple reaction of oxidation of ammonia. Gopalarao and Murty in a subsequent part (*J. Indian Chem. Soc.*, 1941, **18**, 127) have adduced further support for the mechanism already proposed (*vide* Part I). In the publications referred to, it was stated that the photosensitised oxidation of ammonia is a heterogeneous catalytic reaction taking place at the surface of titania under the influence of light. The ammonia adsorbed on the surface of titania interacts with the same under the influence of light, the titania being reduced to a lower oxide. The titanium dioxide is regenerated from the lower oxide by the action of atmospheric oxygen. In view of the importance of surface in this reaction it appeared to us that it would be of considerable interest to study the photosensitised oxidation of ammonia using colloidal titania as the photosensitiser.

EXPERIMENTAL.

The source of ultraviolet light is a Hereaus quartz-mercury vapour lamp worked on 220 volts D.C. at 3.0 amperes. The arc was cooled by working a fan in the neighbourhood. The light was condensed and rendered parallel with the help of a quartz condenser on to the reaction cell, which was a quartz cylindrical vessel with two plane parallel sides of diameter 4 cm. The cell was fitted with a ground-in stopper and has a capacity of 40 ml. The cell was mounted inside a thermostat provided with two windows fitted with quartz plates. Distilled water was circulated through this thermostat from another bigger thermostat of Lowry type by means of a circulating pump. Temperature was controlled to $\pm 0.1^\circ$.



Preparation of Colloidal Titania.—The methods so far developed for the preparation of hydrous titanium dioxide sol give positively charged sols. Graham prepared a hydrous titania sol by dialysis of an 1% solution of the oxide in dilute hydrochloric acid. Bhatia and Ghosh (*J. Indian Chem. Soc.*, 1930, 7, 687) prepared a sol containing 15 g. of TiO_2 per litre by dropping titanium tetrachloride slowly into water at 18° followed by dialysis. Freundlich and Kross (*Kolloid Z.*, 1930, 52, 37) prepared sols, containing 440 to 640 g. per litre by hydrolysis of titanitic sulphate, washing the hydrous oxide free from sulphate with ammonia, and finally peptising with as small an amount of hydrochloric acid as possible. In these sols both H^+ and Ti^{+++} are the stabilising ions. The sols are, therefore, positively charged. As positively charged sols are coagulated by the addition of dilute aqueous ammonia, the following method for the preparation of a hydrous titanium dioxide sol, containing negatively charged particles, was adopted. Merck's titanium tetrachloride was dissolved in water containing hydrochloric acid and the solution treated with excess of aqueous ammonia in the cold in order to precipitate the whole of the titanium dioxide as the so-called orthotitanic acid. The precipitate was freed from electrolytes first by decantation and then by washing repeatedly on the filter. When the wash gave no further test for chlorides, the precipitate was suspended in distilled water, contained in a stoppered Jena bottle. A small amount of "ammonia fort" was added and the bottle shaken vigorously for a long time until the hydrated titania was peptised and passed into colloidal condition. This was then filtered and carefully dialysed to free it from most of the ammonia. It was found that a small amount of ammonia was necessary for the stability of the hydrosol. This sol contains negatively charged particles and is quite stable in the presence of excess of ammonia. The concentration of the sol was determined by evaporating off a known volume of the sol in a weighed dry silica dish and strongly igniting, cooling and reweighing. The increase in weight of the dish gives the weight of titanium dioxide present in the known volume of the colloid. In this way it was found that the sol contained 0.45 g. of TiO_2 per litre.

*Photosensitised Oxidation of Ammonia in Aqueous Solution
in the total Ultraviolet Light.*

20 Ml. of $N/2$ or of another strength of aqueous ammonia solution were taken in the reaction cell and 20 ml. of the hydrosol of titania added,

The cell was then closed with the stopper and the contents shaken and exposed to light from a quartz-mercury vapour lamp as already described for the requisite length of time. The exposure was then stopped, and the contents transferred into a clean conical flask. The colloidal titania was coagulated by the addition of a small quantity of pure solid barium chloride. The solution was then filtered and the nitrite content in the filtrate determined by the Griess-Ilosvay colorimetric method.

TABLE I.

Progress of reaction with time.

Temp. = 30.3°.

NO ₂ -N per litre.			NO ₂ -N per litre.		
Time.	N/4-ammonia.	N/8-ammonia.	Time.	N/4-ammonia.	N/8-ammonia.
8 hrs.	1.22 mg.	1.06 mg.	32 hrs.	4.74 mg.	4.13 mg.
16	2.36	2.01	40	6.10	5.16
24	3.52	3.04			

Table I shows that the amount of nitrite formed increases in direct proportion to the time of exposure. In the absence of titania the amount of nitrite formed in 20 hours was found to be equivalent to 0.11 mg. of nitrite-nitrogen per litre with an N/4 solution. In the presence of titania it will be about 3.06 mg. These results clearly show the photosensitising action of titania. In the following table are recorded the results on the effect of the variation of the concentration of ammonia on the rate of reaction.

TABLE II. =

Influence of concentration of ammonia.

Exposed for 10 hrs. TiO₂ = 0.0090 g. in 40 ml. soln.

Conc. of ammonia.	NO ₂ -N per litre.	Conc. of ammonia.	NO ₂ -N per litre.	Conc. of ammonia	NO ₂ -N per litre.
2.5 × 10 ⁻¹ N	1.53 mg.	1.5625 × 10 ⁻²	1.12 mg.	4.8828 × 10 ⁻⁴	0.55 mg.
1.25 × 10 ⁻¹	1.32	7.8125 × 10 ⁻³	1.03	2.4414 × 10 ⁻⁴	0.50
0.25 × 10 ⁻²	1.21	1.9531 × 10 ⁻³	0.82	1.2207 × 10 ⁻⁴	0.44
3.125 × 10 ⁻²	1.15	9.7655 × 10 ⁻⁴	0.76	* 6.1034 × 10 ⁻⁵	0.41

From Table II it is evident that the photosensitised oxidation of ammonia is a reaction of zero order as the reaction rate is very nearly independent of the concentration of ammonia. Moreover, for a very large change in the concentration of ammonia, the change in the rate of reaction is only very slight. For instance, when the concentration is decreased from $2.5 \times 10^{-1}N$ to $1.562 \times 10^{-2}N$, the amount of NO_2-N formed in 10 hours changes from 1.53 mg. to 1.12 mg, a change of only 28%. If the reaction were unimolecular, it would have effected a 1600% change.

Influence of Electrolytes.

The hydrous titanium dioxide sol, used in the experiments, contained negatively charged micelle and was coagulated by addition of suitable concentrations of positive ions like K^+ , Ba^{++} , etc., obtained from their salts. It has been suggested by Gopalarao (*loc. cit.*) that the photosensitised oxidation of ammonia is a heterogeneous catalytic reaction occurring at the surface of the particles of the photosensitiser and that adsorption plays an important part. During coagulation of a sol by a neutral salt agglomeration of the smaller colloidal particles into bigger aggregates is attended with large decrease in the effective surface. As the reaction studied is a photochemical one, we should select such salts as would not interfere with the absorption of light. In the following table are reported the typical results obtained with varying concentrations of potassium and barium chlorides.

TABLE III.

10 ml. of $N/2$ ammonia solution + 10 ml. of hydrous TiO_2 sol + electrolyte solution + water to make up the total volume to 40 ml.

Exposure = 5 hrs. Temp. = 30.3° .

Potassium chloride.				Barium chloride.			
Electro- lyte conc.	NO_2-N per litre.	Electro- lyte conc.	NO_2-N per litre.	Electro- lyte conc.	NO_2-N per litre.	Electro- lyte conc.	NO_2-N per litre.
*	0.59mg. $37.5 \times 10^{-3}M$		0.45mg. $5.0 \times 10^{-5}M$		0.49 mg. $50.0 \times 10^{-5}M$		0.26 mg.
$5.0 \times 10^{-3}M$	0.59	50.0×10^{-3}	0.45	10.0×10^{-5}	0.48	75.0×10^{-5}	0.20
12.5×10^{-3}	0.58	75.0×10^{-3}	0.45	20.0×10^{-5}	0.44	10.0×10^{-4}	0.19
25.0×10^{-3}	0.51	125.0×10^{-3}	0.45	25.0×10^{-5}	0.38	25.0×10^{-4}	0.19

* When no electrolyte was used.

The results in the foregoing table show that the decrease in the extent of the surface of the photosensitiser, occasioned by the addition of electrolytes, results in a decrease in the reaction rate. With any electrolyte, increasing concentration causes a progressively diminishing rate until a steady limiting rate is attained. When this point is reached, a further increase in the concentration of the electrolyte does not produce a further diminution in the rate of oxidation. The concentration that produces the limiting rate is approximately the same with Na^+ from NaCl , K^+ from KCl and NH_4^+ from NH_4Cl . A point of great significance arising from this investigation is that the concentration of divalent ions Ba^{++} or Sr^{++} required to lower the reaction rate to the limiting value is much lower than with univalent ions like Na^+ and K^+ . Further, it is also to be noted that the limiting rate with divalent ions is lower than that reached with univalent ions.

Effect of Varying the Amount of the Photosensitiser.

In the following table are reported the results obtained, when the amount of photosensitiser was varied by taking varying volumes of the hydrous titan ia sol, while keeping the concentration of ammonia constant.

TABLE IV.

Concentration of ammonia = $N/8$. Temp. = 30.3° . Exposed for 5 hrs.

TiO_2 in 40 ml. (g.)	...	0.01350	0.01125	0.00900	0.00675	0.00450
$\text{NO}_2\text{-N}$ (mg. per litre)	...	0.54	0.62	0.71	0.57	0.53

Table IV shows that increase in the amount of the photosensitiser increases the rate of reaction up to a certain limit beyond which a further increase produces a diminishing rate of reaction. Similar results are often noticed in other photosensitised reactions by other investigators.

Temperature Coefficient of the Reaction.

The required temperature was maintained to $\pm 0.1^\circ$ by circulating water from a big Lowry type thermostat through the smaller thermostat in which the reaction cell is mounted.

TABLE V.

Conc. of ammonia = $N/8$. Photosensitiser = 0.0090 g. per 40 ml. soln.
Exposed for 8 hrs.

Temp.	Nitrite-nitrogen per litre.			
	8 hrs	16 hrs.	24 hrs.	32 hrs
30°	1.06 mg	2.01 mg.	3.04 mg.	4.13 mg
40°	1.22	2.40	3.69	4.83
50°	1.24	2.45	3.68	4.87

The temperature coefficient $K_{40^\circ}/K_{30^\circ} = 1.2$ and $K_{50^\circ}/K_{30^\circ} = 1.0$.

DISCUSSION.

The results presented in this paper support the conclusion that the photosensitised oxidation of ammonia occurs as a heterogeneous photocatalytic reaction at the surface of titania. That the extent of surface is a determining factor is shown by the fact that the rate of reaction is diminished by decreasing the surface of the colloidal titania by the addition of suitable concentrations of electrolytes. The electrolytes added agglomerate and coagulate the colloid, thereby decreasing the available surface. They also tend to displace the adsorbed ammonia from the surface of the photocatalyst. That an interfacial factor is truly operating is conclusively shown by the result that the degree of inhibition produced by univalent ion like that of Na^+ is much less than that produced by the divalent Ba^{++} ion. A heterogeneous photochemical reaction, though very interesting because of its novelty, is somewhat complex and presents a variety of interesting aspects from the theoretical standpoint. We have to take into account the adsorption of ammonia on the surface of the photocatalyst, the spectral sensitivity of the photocatalyst, the intensity of the light, etc.

In Part II of this series it has been shown that ammonia is very tenaciously adsorbed by titania. When adsorption is strong it will be noticed from the Langmuir adsorption isotherm

$$U = \frac{K_2 C}{K_1 C + 1}$$

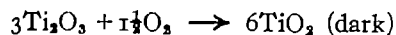
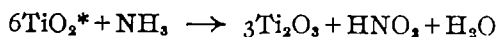
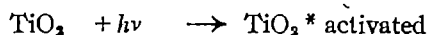
that when, C , the concentration of ammonia is high, $K_1 C$ will be very large compared to unity so that the amount adsorbed,

$$U = \frac{K_2 C}{K_1 C} = \frac{K_2}{K_1} = \text{constant.}$$

Now the velocity of the reaction will be proportional to the active mass of the substance adsorbed and hence in a position to react. When adsorption is strong it is seen that the amount adsorbed is practically constant and independent of the concentration of the ammonia in the solution. Hence the reaction velocity should also be independent of the concentration of ammonia in the solution; in other words, the reaction should exhibit the characteristics of a zero molecular reaction. That this is the case is shown by the results recorded in Table II.

Increasing the surface of the heterogeneous catalyst by increasing the amount of colloidal titania also increases the speed of the reaction up to a certain limit as shown by the results in Table IV. This fact also indicates a possible chemical reaction between the photosensitiser and ammonia. Moreover, it has been shown that the formation of nitrite from ammonia occurs in the presence of titania even in the complete absence of oxygen.

A molecule of titania on the surface gets activated due to absorption of a quantum of radiation. The photoactivated titania then oxidises ammonia to nitrous acid, getting itself reduced to titanous oxide Ti_2O_3 or TiO . The titanous oxide then undergoes rapid oxidation by the dissolved oxygen, thus regenerating the photosensitiser. For this reaction to occur there must be an intimate association between the molecules of the photosensitiser and ammonia, and this association is secured by adsorption.



That photoactivated titania possesses marked oxidising properties is indicated by the work of Benrath (*Z. wiss. Photochem.*, 1915, **14**, 217) and Benrath and Obladen (*ibid.*, 1922, **22**, 65) who showed that titanium dioxide is reduced in light in the presence of alcohol or oxalic acid. Renz (*Helv. Chim. Acta*, 1921, **4**, 961) also showed that while titanium dioxide alone is stable towards light, it becomes markedly photosensitive in the presence of organic substances, particularly glycerol. Goodeve and Kitchener (*Trans. Faraday Soc.*, 1938, **34**, 1) concluded from a study of the fading of "Chlorazol sky Blue FF" adsorbed on titanium dioxide in the presence of light from the quartz-mercury vapour lamp, that the rate of bleaching of the dried sample exposed in vacuum is the same as that of the undried sample in the presence of air. Their results indicate that the bleaching of

the dye is a process of oxidation by titanium dioxide under the influence of light.

The mechanism here proposed for the photosensitisation by titania is similar to the "carrier-type" of mechanism suggested for some photosensitisers from time to time (*cf.* the mechanism proposed for the sensitised decomposition of oxalate in the presence of ferric chloride as sensitiser, "Photoprocesses in Gaseous and Liquid systems," Longmans, Green and Co., London, 1929).

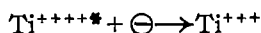
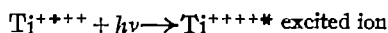
In recent years Goodeve and co-workers have devoted considerable attention to photosensitisation by titanium dioxide (*Trans. Faraday Soc.*, 1937, **33**, 340; 1938, **34**, 570, 902). They have tried to explain the mechanism of the photosensitisation by solids making use of the concept of "exciton" introduced by Frenkel (*Physikal. Z. Sowjet*, 1936, **9**, 158).

"A quantum of energy, when absorbed by an electron in a crystal, is probably initially localised (in the case of non-conductors). Before it can cause a photochemical change, this energy must pass as a more or less complete unit (Frenkel has termed this unit an "exciton") to the point of contact of the potentially reactive molecular species. In the case of carbon black, or metallic blacks (conductors), such a transfer is exceedingly unlikely to occur owing to disturbance of the free electrons which would lead to degradation of the "exciton" to heat. In a pure crystal of a non-conductor an excited electron is only influenced by electrons of neighbouring molecules and there is very little coupling with the vibrations of the atoms and molecules. Degradation to heat is, therefore, less likely to occur than with carbon black. Two things may happen. The "exciton" may be reradiated as fluorescence of the same or a lower frequency, or it may be passed to a neighbouring electron by resonance between the two. The probability of the transfer of energy between two electrons of identical frequencies separated by the distances occurring in crystals is high. We have, therefore, as a picture of the probable state of affairs subsequent to absorption of a light quantum, a rapid passage of the exciton at random throughout the crystal until it meets a surface where it might cause a chemical change. The "exciton" here is pictured as an excited electronic state, the energy being handed on without actual transfer of the electrons. It may, however, be of the type of excitation found in some photoconductive crystals (*cf.* Hughes, *Rev. Modern Phys.*, 1936, **8**, 294) in which "an ion pair is formed on absorption of light. The positions of the ions (not the ions themselves) may move to the surface, causing oxidation or reduction."

" Many photosensitised reactions take place on the surface of the solid particles, and if an exciton is to produce a photochemical change it must diffuse to this surface. As the diffusion, however, will presumably not have a directional effect towards the surface it will usually travel a distance much greater than that between the original absorption centre and the surface. The exciton may move more readily along a particular axis of the crystal corresponding to greater interaction between the electrons in this direction."

Goodeve imagines the existence of potentially reactive centres on the surface. " A potentially reactive centre consists of a group of atoms which can undergo rearrangement or give up or accept electrons, when provided with the necessary energy. If the equilibrium position of some nucleus changes markedly in the presence of an exciton a rearrangement of atoms may readily be produced when the exciton reaches the potentially reactive centre. On the other hand if the exciton corresponds to a free electron it could readily cause a reduction on reaching a centre on the surface capable of accepting an electron."

In our view it is not necessary to assume the operation of the complex and speculative concept of " exciton " of Frenkel to explain the mechanism of photosensitisation by titanium dioxide. The experimental data of Goodeve and Kitchener (*loc.cit.*) as also the results of Gopal Rao and co-workers can be explained on the simple basis that the surface molecules only of the titanium dioxide particles are photo-active, whilst the interior molecules of titania are completely inactive. An ion of Ti^{++++} in a molecule of TiO_2 on the surface of a particle of titania gets electronically excited on the absorption of a quantum of light. An electron is raised to a higher energy level and according to Franck and Haber (*Sitz. Preuss. Akad. Wiss.*, 1931, 250) such a molecule, atom or ion which possesses an unoccupied electronic level has a tendency to take up an electron ; hence it will exert an oxidising action on substances that are adsorbed on the surface, the molecules or atoms of which donate electrons and get oxidised. Oxidation primarily consists in loss of electrons and reduction in a gain of electrons.



That the absorption of light by titania is due to a titanium ion which is raised to an excited level is made probable by the observation of Goodeve and Kitchener (*Trans. Faraday Soc.*, 1938, **34**, 902) that the threshold of absorption for solid titania lies in the same region of the spectrum as that of the ions in solution.

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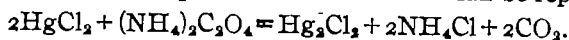
Received April 15, 1941.

MAGNETISM AND CATALYSIS. PART IV. CATALYSIS OF THE REACTION BETWEEN AMMONIUM OXALATE AND MERCURIC CHLORIDE BY FERRIC IONS.

By S. S. BHATNAGAR, P. L. KAPUR, ANAND SWAROOP BHATNAGAR AND
BRAHM PRÁKASH.

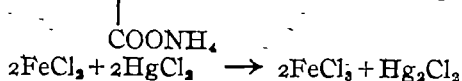
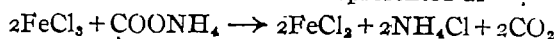
The influence of ferric ions in catalysing the reaction between ammonium oxalate and mercuric chloride has been studied from magnetic standpoint. Results indicate that a new intermediate compound having a lower paramagnetic susceptibility value than that of ferric chloride is formed. It has not, however, been possible to ascertain definitely whether this intermediate compound is ferrous chloride or ferrous oxalate.

Much speculation is rife as regards the mechanism of the catalytic reaction between mercuric chloride and ammonium oxalate. Planche (*J. Pharm.*, 1815, 49), Becquerel and Beny ("La Lumière ses causes et ses effets" 1868), and later on Eder investigated the reaction thoroughly and showed that the reaction is a photochemical one and can be represented as

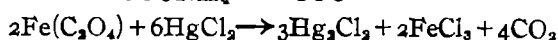
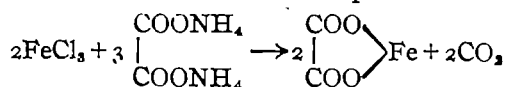


Kastle and Beatty (*Amer. Chem. J.*, 1900, 24, 182) showed that this reaction is accelerated by the presence of ferric and uranyl salts whereas it is retarded by the presence of chromates and chromic acid.

Winther (*Z. wiss. Phot.*, 1909, 7, 409; 1910, 8, 237, 197) suggested that the reaction in the Eder's solution proceeds through the intermediate formation of ferrous chloride which further reduces mercuric chloride to mercurous chloride. The reaction can be represented as



Winther (*ibid.*, 1919, 17, 409) later on studied in detail the influence of various catalysts on the reaction and observed that ferric salts, when present in small concentrations, accelerate the reaction whereas when they are present in larger concentrations, they act as inhibitors. Winther suggested that in the presence of catalysts, the reaction proceeds through the formation of ferrous oxalate which in its turn reduces mercuric chloride to mercurous chloride. The whole mechanism could be represented as



Berger (*Rec. trav. chim.*, 1921, **40**, 387) carried out systematic study of this reaction and concluded the view that the reaction takes place between the mercuric and oxalate ions as untenable. He, however, completely neglected the influence of iron salts in explaining his view.

The present investigation has thus been undertaken to clarify the reaction mechanism from magnetic standpoint.

EXPERIMENTAL.

The purity of the materials used was of a very high order. B. D. H. analytical reagents were purified and used. In the case of solutions, susceptibility has been calculated with the help of the relation

$$\chi_{\text{soln}} = \chi_{\text{salt}} \times C_{\text{salt}} + \chi_{\text{solvent}} (1 - C_{\text{salt}}).$$

Specific susceptibilities of the solution of the same order of strength as were to be used in the reaction were also determined and this relationship found to be valid.

The following solutions were prepared in conductivity water of which the susceptibility value had been determined: (i) 0.10N-mercuric chloride; (ii) 0.101N-ammonium oxalate. In mixing up the solution, 100 c.c. of 0.10N-mercuric chloride were taken in a flask and 99 c.c. of 0.101N-ammonium oxalate were added followed by 1 c.c. of FeCl_3 of known strength.

The whole mixture was then immediately exposed to sunlight for definite periods of time. Three different samples were exposed each time and six readings were taken at different intervals. After the required exposure the flasks were carried immediately to a dark room and connected to a vacuum pump to remove any dissolved carbon dioxide evolved during the reaction. The filtrate was made up to 250 c.c. in conductivity water. All these operations were carried out in a dark room under red light. The susceptibility of these solutions was determined on a modified form of Guoy's balance. Exposure of sunlight was avoided on account of the reaction being photochemical. It was observed, however, that if great care was not taken in keeping the exposed samples, either when estimating their constituents or when determining their susceptibility, in complete absence of sunlight, the readings obtained were not reproducible. The chemical analysis of these solutions was also, carried out side by side, by estimating the unreacted oxalate by the usual potassium permanganate method and the unreacted HgCl_2 by estimating it as HgS .

The results of these determinations are tabulated in Table II. The theoretical values of χ were calculated on the following data (Table I).

TABLE I.

Compound.	$\chi \times 10^6$.	Reference.
Ammonium oxalate	-0.527	(Author's)
Mercuric chloride	-0.298	"
Ferrous oxalate	+67.48	"
Ferrous chloride	+101.2	(International Critical Tables)
Ferric chloride	+82.05	(Author's)
Ammonium chloride	-0.640	(International Critical Tables)

TABLE II.

HgCl₂ = 100 c.c. Am. oxalate = 99 c.c. FeCl₃ = 1 c.c. Total vol. = 200 c.c.

Time (min.).	Soln. containing unreacted oxalate (c.c.).	Chemical analysis.		χ of solution calc. on mixture law.	χ of solution observed.	χ of conductivity water.	FeCl ₃ (%).	Volume of final solution (c.c.)
		C.c. of N/10.20 KMnO ₄ used.	Normality of unreacted oxalate.					
				I	II			
0 50	51.5	0.101	-0.709 $\times 10^{-6}$	-0.709 $\times 10^{-6}$	-0.708 $\times 10^{-6}$	-0.729 $\times 10^{-6}$	1.002	250
3 50	17.25	0.033	-0.715	-0.715	-0.716	-0.721	1.002	250
6 50	11.85	0.023	-0.721	-0.722	-0.723	-0.728	1.002	250
12 50	10.25	0.020	-0.718	-0.721	-0.721	-0.729	1.001	250
60 50	4.70	0.009	-0.716	-0.716	-0.718	-0.729	1.076	250
360 50	2.15	0.004	-0.710	-0.710	-0.710	-0.727	1.043	250

DISCUSSION.

In the case of this reaction the magnetic data (Table II) reveal that :—

- At initial stages the mixture law is obeyed.
- At intermediate stages, there is a distinct tendency of increase in the susceptibility values of the solution towards diamagnetism. This is to an extent of 0.43%.

- At the final stages, the mixture law again holds good.

These results indicate that a new intermediate compound having a lower paramagnetic susceptibility value than that of the ferric chloride is formed in the intermediate stages.

According to the two views put forward by Winther, the reaction takes place either through the formation of ferrous oxalate or ferrous chloride as an intermediary compound.

The molecular susceptibilities of ferric chloride, ferrous chloride and ferrous oxalate are 13333×10^{-6} , 12852×10^{-6} and 9717×10^{-6} respectively.

If the reaction proceeds through the formation of ferrous oxalate as an intermediary compound, and whole of the ferric chloride is converted to ferrous oxalate, which is generally not the case, the susceptibility of the solution ought to show a marked increase in the diamagnetism of the solution. On the other hand, if the reaction proceeds through the formation of ferrous chloride the susceptibility of the solution would not differ much from that when ferric chloride is present there and this may be responsible for the small difference between the experimental and calculated susceptibility values of the reacting solutions. It may be argued that in the reaction under investigation, whole of the ferric chloride is not converted to ferrous oxalate as is generally the case in catalytic reactions and thereby the effect produced on the magnetic properties of the solution due to the formation of ferrous oxalate as an intermediary compound is not appreciable, and thus the difference between the observed and calculated susceptibility values of the solution is not marked. Formation of ferrous oxalate as an intermediary compound in the reaction is further supported by Winther who observed that ferrous oxalate reduces mercuric chloride even in the dark at room temperature.

From the magnetic data, although it is not possible to say definitely whether ferrous chloride or ferrous oxalate is formed as an intermediate compound yet it shows that the reaction is definitely proceeding through the formation of intermediate compound.

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Received April 3, 1941.

MICRO ANALYTICAL METHOD FOR THE ESTIMATION OF FERROUS AND FERRIC IRON IN MINERALS.

BY JYOTIRMOY DAS-GUPTA.

A micro-analytical method for the estimation of ferrous and ferric iron in the same sample of mineral has been proposed. The method consists in decomposing the mineral with a mixture of hydrochloric and hydrofluoric acid in a pyrex glass vessel and titrating the ferrous iron in the resulting solution with ceric sulphate and the total iron subsequently with titanous chloride. Two sets of redox indicators have been used namely, (i) ferrous *o*-phenanthroline complex with methylene blue and (ii) *N*-phenylanthranilic acid with potassium thiocyanate. The method has been successfully used for the micro-estimation of ferric and ferrous iron in minerals such as magnetite, ilmenite, etc.

Pichler first developed a method for the micro-estimation of ferrous iron with diphenylamine as internal indicator in which an addition of extra ferric chloride was needed for a sharp end-point, and the method gave a maximum relative error of 3% (*Z. anal. Chem.*, 1928, **73**, 209). Kolthoff and Server (*J. Amer. Chem. Soc.*, 1930, **52**, 4190; 1931, **53**, 2609) studied the properties of various redox indicators and reported better result with diphenylsulphonic acid. Ferrous *o*-phenanthroline complex has been worked out and has also been employed as an indicator for the micro-estimation of iron (Walden, Hammet and Chapman, *ibid.*, 1933, **55**, 2649; Fryling and Tooley, *ibid.*, 1936, **58**, 826). An indicator correction was, however, found to be necessary by the latter workers. A correction for the silver reductor in which the iron solution was reduced was also found unavoidable.

Following Karsonov, Syrokonsky and Stiepin (*J. Amer. Chem. Soc.*, 1936, **58**, 928) found *N*-phenylanthranilic acid a better substitute for ferrous *o*-phenanthroline complex as it requires no indicator correction.

A method for the purpose of estimating both the ferrous and ferric iron in one and the same solution and its adaptation to micro scale is described in the present paper using ceric sulphate and titanous chloride reagents with two sets of different redox indicators like (i) *o*-phenanthroline ferrous complex with methylene blue, and (ii) *N*-phenylanthranilic acid with potassium thiocyanate solution. No indicator correction is necessary. *N*-phenylanthranilic acid was used as an indicator for the estimation of ferrous iron and potassium thiocyanate when estimating the total iron. Boric acid was added before the titration as proposed by Barneley (*J. Amer. Chem. Soc.*, 1915, **37**, 148) to remove the disturbing influence of the excess of hydrofluoric acid used to dissolve the mineral. Small quan-

ties of iron of the order of 10^{-2} mg. present in the mineral both in the ferrous and ferric state could be estimated by this method with good results.

EXPERIMENTAL.

The mineral (20—50 mg.) was carefully weighed into a pyrex conical flask (100 c.c.) previously filled with pure carbon dioxide, which was purified by passing through two wash bottles containing (i) stannous chloride to remove any oxidising substances, and (ii) sodium bicarbonate to remove impurities like SO_2 , H_2S , etc. After passing the gas for a few minutes hydrofluoric acid (1-2 c.c.) and concentrated hydrochloric acid (10 c.c.) were quickly introduced into the flask and it was heated on an electric heater to about 50° . The ore dissolved in a few minutes (it takes a longer time when the titanium content is high), the flask was cooled and the current of carbon dioxide increased. To the solution in the flask about 35 c.c. of 5% boric acid solution (in $N/2$ HCl) were added and the solution diluted with water (previously boiled to remove dissolved oxygen) so that the acid strength was about 2 N . One drop of ferrous *o*-phenanthroline (0.025*M*) was added as an internal indicator and the whole was titrated with standard ceric sulphate solution from a microburette. Before the titration a few drops (about 0.5 c.c.) of syrupy phosphoric acid was added to get a sharp end-point. When the end-point was reached 1 drop of methylene blue was added and the whole solution was again titrated with standard titanous chloride.

Sharp end-point with methylene blue could be obtained only at 35° . Addition of 1 or 2 drops of 10% sodium salicylate solution with methylene blue gives the same effect at lower temperatures.

After both the titrations were over and the proper indicator correction applied from blank experiments, the ferric iron present in the solution was calculated.

With ferrous *o*-phenanthroline and methylene blue a sample of magnetite gave the results shown in Table I A.

TABLE I.

A.			B.		
Ore taken.	Ferrous iron.	Total iron.	Ore taken.	Ferrous iron	Total iron.
0.03040 g.	22.4%	67.0%	0.02876 g.	22.35%	67.3%
0.2310	22.3	67.2	0.02279	22.3	67.2
			0.01950	22.2	67.1

Sample from the same magnetite was analysed as before but with phenylanthranilic acid and potassium thiocyanate as indicators. Without any indicator correction and without the addition of phosphoric acid the results shown in Table I B were obtained.

The magnetite, when analysed by the standard method using standard potassium dichromate solution and diphenylamine, was found to contain ferrous iron to the extent of 22.3% and total iron, 67.3%.

Indicator Correction.—With ceric sulphate and ferrous *o*-phenanthroline complex, when the standard titrating solution is sufficiently dilute, indicator correction is essential as evident from Table II.

TABLE II.

Ferrous <i>o</i> -phenanthroline (0.025 <i>M</i>) taken (c.c.)	...	0.01	0.02	0.028	0.03
Ceric sulphate required to discharge the colour (c.c.)	...	0.06	0.11	0.16	0.17

The indicator correction graph when plotted gives a straight line.

Table III shows that no indicator correction is necessary with *N*-phenylanthranilic acid. About 5 drops of the indicator (1.07 g. of the acid with 10 g. of sodium carbonate per litre) was found to give a sharp end-point.

TABLE III.

<i>N</i> -Phenylanthranilic acid (c.c.)	...	0.05	0.10	0.15	0.20	0.30	0.35	0.40
Ceric sulphate soln. required for colour change (c.c.)	.	0.01	0.01	0.01	0.01	0.01	0.01	0.01

No phosphoric acid was added in the above titrations.

Similarly with methylene blue and titanous chloride an indicator correction is essential as the dye is quantitatively reduced by the titanous chloride solution. Blank experiments demonstrate that these indicators used in combination exert no mutual effect upon one another. Different amounts of ferrous *o*-phenanthroline were taken and after the colour was discharged with ceric sulphate, one drop of methylene blue (1%) and two drops of sodium salicylate (10%) were added and the solution was again titrated with titanous chloride solution.

TABLE IV.

Ferrous <i>o</i> -phenanthroline added (c.c.) ...	0.012	0.02	0.03	0.04	0.06
Titanous chloride required for 1 drop of methylene blue (c.c.) ...	0.08	0.08	0.09	0.08	0.09

In all the above experiments about $N/100$ -ceric sulphate solution in dilute sulphuric acid was used. Titanous chloride when prepared in $2N$ -hydrochloric acid solution was found to be more stable.

The Micro Method.—Pure ferrous ammonium sulphate carefully weighed in a microbalance, was dissolved in $2N$ -hydrochloric acid, 0.05 c.c. of phosphoric acid (when ferrous *o*-phenanthroline was used as indicator) was added to obtain a sharp end-point. Hydrofluoric acid (1 c.c., 40%) and boric acid solution (35 c.c.) were introduced in to the flask. Hydrochloric acid was added to bring the solution to $2N$ and titrated first with ceric sulphate and then with titanous chloride using the two sets of redox indicators previously mentioned. The results are shown in Table V.

TABLE V.

Indicator : (i) Ferrous *o*-phenanthroline, and (ii) methylene blue.

Ferrous ammonium sulphate taken.	Fe calc.	Fe Found with $\text{Ce}(\text{SO}_4)_2$.	with TiCl_3 .
4.541 mg.	0.6485 mg.	0.6462 mg.	0.6460 mg.
4.671	0.6685	0.6658	0.6658
4.469	0.6380	0.6470	0.6460
4.470	0.6380	0.6400	0.6390

(i) Phenylanthranilic acid (1.07 g. with 10 g. of Na_2CO_3 per litre), and (ii) potassium thiocyanate (10%).

4.124 mg.	0.589 mg.	0.600	0.592
3.827	0.546	0.553	0.546
7.678	1.096	1.092	1.092
4.173	0.596	0.614	0.601
3.343	0.474	0.477	0.481
2.735	0.391	0.396	0.390

In the above titrations no phosphoric acid was added. The results found are quite satisfactory.

In the case of a mineral the ore was crushed in an iron mortar and purer pieces were sorted out with the help of a pair of tongs. The small pieces were then purified with the help of a horse shoe magnet. They were again crushed and sieved by a 150-mesh sieve. The powdered ore was then further purified by magnetic separation. Micro quantities of the ore (as well as semimicro and macro quantities) were weighed out in a 100 c.c. pyrex Erlenmeyer flask (Soule, *J. Amer. Chem. Soc.*, 1928, **50**, 1691) filled with pure carbon dioxide as previously stated. Hydrofluoric acid (2-3 c.c.) and about 10 c.c. of concentrated hydrochloric acid were added and the flask was heated in an electric heater. In the decomposition of the ore hydrochloric acid was found to be more convenient than sulphuric acid specially in the case of magnetite (*cf.* Adam, *J. South African Chem. Inst.*, 1925, **8**). The ore decomposed in a few minutes, the solution was cooled down and the rate of carbon dioxide flow increased. Boric acid solution (35 c.c., 5% in $N/2$ -hydrochloric acid solution) was added and the solution was kept about $2N$ (only boiled and cooled water was used when dilution was necessary). The solution was titrated in a current of carbon dioxide. Phenylanthranilic acid (5-6 drops of the solution) and potassium thiocyanate (10 c.c. of 5% solution) were used as indicator for which no indicator correction was required. The results are recorded in Table VI.

TABLE VI.

A. Magnetite.			B. Ilmenite.		
Amount taken.	Fe'' [by $Ce(SO_4)_2$]	Total Fe (by $TiCl_3$).	Amount taken.	Fe'' iron [by $Ce(SO_4)_2$].	Total iron [by $TiCl_3$].
3.310 mg.	22.6%	67.2%	1.207 mg	28.6%	43.37%
4.274	22.4	67.0	2.791	28.2	43.55
3.165	22.6	67.1	2.666	28.2	43.60
1.884	22.5	67.3	3.781	28.4	43.20
Mean	22.5	67.2	Mean	28.35	43.43
	22.3*	67.0		28.40*	*43.5
				28.45†	†43.5

* By Macro method.

† By Semi-micro method.

Ilmenite.

The same procedure was adopted in the analysis of ilmenite. Longer time was required in the decomposition of the mineral probably due to the higher titanium content.

The method can thus be conveniently used for the micro estimation of ferrous and ferric iron present in the same mineral sample.

Restriction—The method is applicable only when the interfering substances like trivalent vanadium etc. are absent.

My best thanks are due to Dr. P. B. Sarkar for suggesting the problem and for laboratory facilities.

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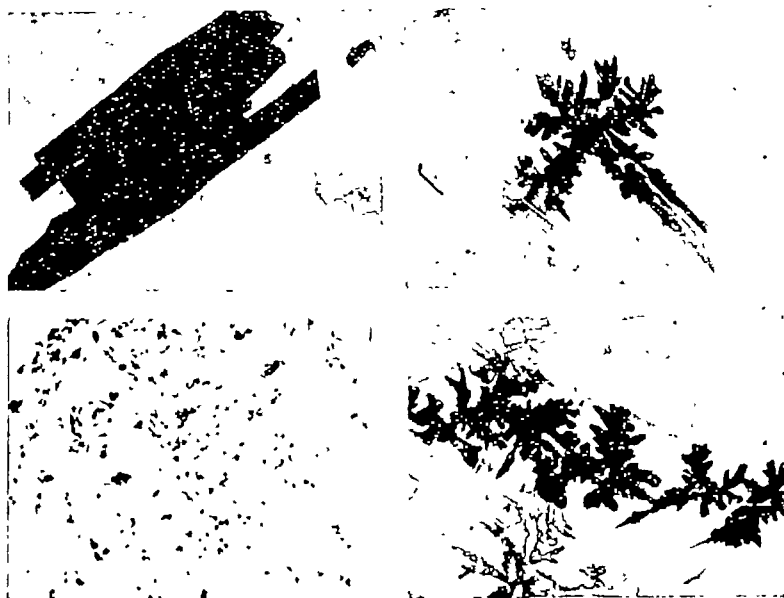
Received May 12, 1941.

MICROCHEMICAL INVESTIGATIONS ON SPOTTED MUSCOVITE MICA.

By JYOTIRMOY DAS-GUPTA.

The chemical nature of some black spots often found in the muscovite mica of Indian origin has been investigated and from their micro-analytical study it has been proved that they consist of crystallised magnetite imbedded between the mica sheets.

It has been observed that some pieces of the muscovite mica from Nellore (India) contain some minerals imbedded between thin sheets of mica which appear like tiny specks scattered all over the surface. The exact nature of these spots were not known probably due to analytical difficulty resulting from their fineness as well as for their inseparable nature from the main body, as can be judged from the attached photographs and microphotographs. These spots have been investigated in the present paper with the help of a micro method described in an earlier communication.



A qualitative micro analysis of the spotted and the colourless portions of the same piece of mica indicates a difference in their iron contents only and absence of elements like titanium, manganese, etc. This seems to suggest that they might consist of haematite or magnetite particles and obviously the latter as both the ferrous and ferric iron are present in them.

This assumption has further been supported by the paramagnetic nature of these spotted parts when compared with the colourless portions and also from the ferrous/ferric ratio as determined by the micro-volumetric method. They are, therefore, regarded as fine particles of crystallised magnetite imbedded between the mica films.

EXPERIMENTAL.

Pieces of mica representing only the stained parts and free as far as possible from the colourless portions were dissolved in a mixture of hydrofluoric and concentrated hydrochloric acid (1 c.c. : 5 c.c.) and analysed for ferrous and ferric iron by the micro volumetric method described in the previous paper (p. 375).

In the titrations for iron, indicator correction was applied when the mica spots were analysed. Ceric sulphate solution (0.009880N in dilute sulphuric acid) and $N/150$ titanous chloride (in 2N hydrochloric acid) solution were used. The solution required for the titration was of the order of 10^{-1} c.c. The following results were obtained :—

Ferrous iron (mg.) (ceric sulphate)	...	0.0108	0.0673	0.0651	0.0670	0.1308
Total iron (mg.) (titanous chloride)	...	0.0327	0.2010	0.2010	0.2010	0.3912

The above data show the ratio between ferrous and total iron present in the spots to be about 1:3, a fact which definitely proves the mineral crystallised between the thin films of the mica to be composed of magnetite.

My thanks are due to Dr. P. B. Sarkar for helpful suggestion and laboratory facilities.

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Received May 12, 1941.

COMPLEX FORMATION BY ASCORBIC ACID WITH FORMALDEHYDE.

By P. V. KRISHNAMURTHY.

Formaldehyde is found to form a complex with ascorbic acid as shown by two independent methods of estimation of ascorbic acid, the titration with dichlorophenol-indophenol and the titration with iodine solution. The complex formation has been found to vary with the p_H of the solution containing the ascorbic acid. Quantitative estimations of formaldehyde also support the above conclusion.

During the study of the influence of various substances on ascorbic acid oxidation it was observed that formaldehyde lessens, to a striking extent, the capacity of ascorbic acid for consuming the 2:6-dichlorophenol-indophenol dye, even in the initial stages, irrespective of the presence or otherwise of added Cu^{+1} . This was found to be interesting, as many substances that occur in plant and animal tissues were on the other hand found to possess inhibitory influence on ascorbic acid oxidation to varying degrees, as reported by Krishnamurthy and Giri (*J. Indian Chem. Soc.*, 1941, 18, 191). Further, it was found strange that such a powerful reducing agent as formaldehyde behaves like this towards ascorbic acid. Hence in this paper are given the results of the study in detail of the effect of formaldehyde on ascorbic acid, in order to settle the mechanism.

EXPERIMENTAL.

For determining the percentage of vitamin that has disappeared on treatment with formaldehyde, 10 ml. of the buffer of the appropriate p_H were kept in a conical flask, the required volume of formaldehyde solution was added along with enough water to make the total volume 20 ml. The mixture was shaken well and kept in an electrically controlled thermostat at 37°. Then 5 ml. of the solution containing 5 mg. of ascorbic acid were added, and after shaking well, 2 ml. of the mixture were pipetted out into 1 ml. of glacial acetic acid and titrated immediately with 2:6-dichlorophenol-indophenol solution from a microburette. For the iodine estimation, 2 ml. of the mixture, added to 1 ml. glacial acetic acid, were titrated with $N/500$ -solution of iodine from a microburette using starch as the indicator. Pure and redistilled formaldehyde was used in this investigation.

Estimation of formaldehyde in the reaction mixture was done according to the following method (Sutton, "Volumetric Analysis," 11th Ed., p. 373). 2 ml. of the reaction mixture were pipetted out into

a conical flask containing 10 ml. of $N/10$ solution of iodine and immediately treated with a solution of sodium hydroxide drop by drop until the liquid became clear yellow. After 10 minutes enough dilute hydrochloric acid was added to liberate the uncombined iodine, which was then titrated back with $N/10$ -sodium thiosulphate solution.

Effect of varying the Concentrations of Formaldehyde on Ascorbic Acid.—The percentage of ascorbic acid disappearing at p_H 5.6 on the addition of formaldehyde initially, as well as after 30 and 60 minutes, was determined both by titration with the indophenol dye and $N/500$ -iodine solution, and the results obtained by both the methods are presented in the following table. Blank experiments were performed and it was found that formaldehyde alone in the reaction mixture under the experimental conditions, does not consume the dye. However, it was found that it takes up 0.15 ml. of iodine solution irrespective of the concentration of the formaldehyde used, and evidently this is required for the production of the blue colour with starch, which was used as the indicator in these titrations.

TABLE I.

$$p_H = 5.6$$

Percentage of ascorbic acid disappearing.

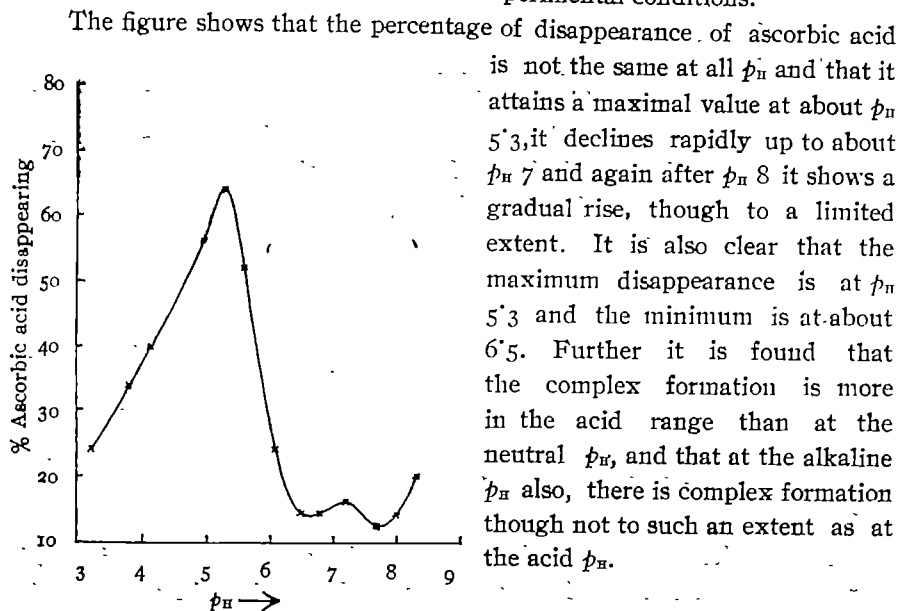
% Conc. of $H\cdot CHO$ in the mixture per 100 ml.	Estimation with I_2 .			Estimation with dye.		
	0 min.	30 min.	60 min.	0 min.	30 min.	60 min.
0	—	34%	50%	—	32%	52%
0.072 g.	4%	34	48	6%	36	50
0.144	8	34	48	10	38	54
0.288	12	36	50	16	38	52
0.364	14	38	50	18	40	54
0.72	30	50	60	38	52	62
1.08	38	56	64	46	58	66
1.44	46	60	66	54	64	70
1.84	52	64	72	64	70	76
3.68	72	80	82	82	86	88
5.52	82	84	88	90	92	92
7.36	82	84	84	88	88	90
9.20	84	88	88	90	92	92

The reaction mixture consisted of 10 ml. of $M/5$ -acetate buffer of p_H 5.6, 5 mg. of ascorbic acid, formaldehyde solution, and water to make up the total volume to 25 ml.

The results in the above table show clearly that there is a decrease in concentration of the ascorbic acid immediately after the addition of formaldehyde. Though this decrease increases with the increase in the concentration of formaldehyde, the ascorbic acid does not, however, completely disappear on the addition of a high concentration of formaldehyde. Further, the disappearance of ascorbic acid is not due to oxidation, as it is

observed only initially, and later with time, it is only gradual. It is clear, therefore, that the disappearance of ascorbic acid initially is not due to oxidation, but must be due to complex formation. These results also show clearly that the percentage of ascorbic acid disappearing after 30 and 60 minutes is not so much as is observed initially, and hence must be due to the spontaneous oxidation of the vitamin. It is also evident that after the initial complex formation, the rate of oxidation of the residual vitamin is almost the same as would be observed with ascorbic acid by itself.

Effect of Formaldehyde on Ascorbic Acid at Different p_H .—The effect of formaldehyde on ascorbic acid at different p_H was studied, and the results thereof are represented graphically. For this also the amount of ascorbic acid disappearing was determined both by titration with the indophenol dye and $N/500$ -iodine solution, from acetate and phosphate buffers of the appropriate p_H . At each p_H it was established that the concentration of formaldehyde does not alter in any way by performing blank estimations under the experimental conditions.



is not the same at all p_H and that it attains a maximal value at about p_H 5.3, it declines rapidly up to about p_H 7 and again after p_H 8 it shows a gradual rise, though to a limited extent. It is also clear that the maximum disappearance is at p_H 5.3 and the minimum is at about 6.5. Further it is found that the complex formation is more in the acid range than at the neutral p_H , and that at the alkaline p_H also, there is complex formation though not to such an extent as at the acid p_H .

It has also been established quantitatively that formaldehyde also undergoes decrease in concentration as a result of the complex formation with ascorbic acid. For this purpose 20 mg. of ascorbic acid were taken in a buffer of p_H 5.6 and treated with formaldehyde, keeping alongside blanks with formaldehyde and ascorbic acid of the same concentrations. The formaldehyde was estimated by the method described, and the amount of iodine used up by ascorbic acid was also simultaneously determined. The

results in Table II show that formaldehyde decreases on treatment with ascorbic acid.

TABLE II.

Ascorbic acid in the blank	20.0 mg.
Formaldehyde in the blank	472.5
Ascorbic acid in the reaction mixture	9.75
Formaldehyde in the reaction mixture	459.3

Similar experiments were performed a number of times and in every case a decrease in formaldehyde concentration was noticed. It is significant, however, that ascorbic acid is never used up completely in the complex formation even though a large amount of formaldehyde is used.

DISCUSSION.

The results presented in this paper show that formaldehyde immediately on addition reduces the concentration of ascorbic acid, as is shown by the reduction in its dye and iodine consuming capacities, and that this is due to complex formation with ascorbic acid.

This observation is of particular interest, since both formaldehyde and ascorbic acid are synthesised and are present in the plant tissues, and perhaps as a result of this complex formation, further syntheses might be brought about. Further, it is noteworthy that this complex formation is dependent on the p_H of the medium, the acid range favouring it considerably, whereas in the neutral range it is minimum, tending to increase in the alkaline range.

Kurin (*Biokhimiya*, 1937, 2, 127) while studying the catalytic effect of vitamin-C in the synthesis of carbon chains observed that the addition of formaldehyde to *iso*-ascorbic acid greatly diminishes the reducing power of the latter, and concluded that apparently an addition product is formed, but adduced no evidence to support his observation. West and Ney (*Science*, 1936, 84, 294) found that ascorbic acid catalyses the conversion of formaldehyde to reducing sugars in presence of calcium hydroxide.

The results show conclusively that ascorbic acid forms a complex with formaldehyde. Acetaldehyde and paraformaldehyde have been found to be without a similar effect.

Further work on the isolation and study of the complex is in progress.

The author acknowledges with thanks the facilities given by Major F. A. B. Sheppard, Principal, Andhra Medical College, Vizagapatam and the interest shown in this investigation by Dr. G. Gopala Rao, and the assistance in the experimental work given by Mr. M. V. Tirumalarao.

OBITUARY

W. L. DAVIES, PH.D., D.Sc., N.D.A., F.I.C.

Born Feb. 23, 1896.

Died May 15, 1941.

William Lewis Davies was born on February 23, 1896. He was educated at Leandile County school and at Clarks College, Swansea and London. He served during the last war (1915-19) and on its termination he returned to his studies at the University of Aberystwith, Wales where he obtained his B.Sc. degree and later National Diploma of Agriculture. He continued studies at the Cambridge University where he obtained M.Sc. and PH.D. degrees. He was employed in the University of Reading as Advisory Agricultural Chemist during 1924-27 and thereafter he worked at the National Institute for Research in Dairying at Reading as Dairy Chemist. He published a large number of papers on various problems connected with dairying on which he was awarded D.Sc. degree by the University of Aberystwith, Wales. From the practical experience of farming and dairying coupled with the theoretical knowledge he had gained at the Universities he wrote his book "Chemistry of Milk", which has been acknowledged as a standard treatise on the subject.

When he came out to India as Director of Dairy Research, Government of India, his chief aim was to study the conditions that will lead to increasing the yield of the ordinary dairy cow. In 1940 he published a brochure on "Indian indigenous milk products" which will be of great interest to the Indian dairying industry. He set himself seriously to work out schemes and prepared a long list of research problems. This work was however, interrupted by his illness in summer of 1940. The present war having intervened, the Government could not grant him the funds for the building and farm but allocated all the same a small amount to start research work in Chemistry and Bacteriology at the Imperial Agricultural Research Institute at New Delhi.

During his short stay in India, he endeared himself to all with whom he came in contact by his unassuming and frank character, honesty of purpose and readiness to help students, research workers, or industrialists and identified himself with the people of the soil. It is a great misfortune that the climate of India was unkind to him who gave his all in her service. He leaves behind in England his wife and a son and a daughter aged respectively 17 and 14.

He was elected a Fellow of the Society in September 1940. During his short stay he contributed the following papers of which two have already been published and the rest are in course of publication in the Industrial and News Edition of the Society's main Journal.

1. The antioxygenic effect of cereal flour paste as a coating on contact wrappers for fatty foods (1940, Vol. III, p. 174)
2. Deterioration of butter during storage. Part I. Development of fishiness (1941, Vol. IV, p. 1)
3. Deterioration of butter during storage. Part II. Development of tallowiness (in press)
4. Deterioration of butter during storage. Part III. Free acidity. (in press)
5. Deterioration of butter during storage. Part IV. Mouldiness and ketonic rancidity.

B. N. K.

N. R. CHATTERJEE, M.Sc.

Born September 4, 1891.

Died June 23, 1941.

Nihar Ranjan Chatterjee was born on the 4th of September, 1891 in Calcutta. After passing entrance Examination from Banka (Bhagalpore) school he joined the Presidency College Calcutta and obtained M.Sc. degree in 1915 standing first in organic group. He was awarded a Government Research Scholarship at the Presidency College and he published several original papers. He had also prepared a thesis entitled "A Constant for the endothermic compounds—the temperature of detonation". In March 1918, he joined the laboratory of Messrs. Smith Stanistreet & Co. as a chemist, and thereafter served the Dacca College for 2 years, first as a demonstrator and subsequently a lecturer in chemistry. He next joined the I.R.F.A. under Sir U. N. Brahmachari. The credit of the discovery of Urea Stibamine was greatly his as he had himself synthesised this compound as well as other compounds of a similar nature, which were all tested by Sir Upendra Nath. Mr. Chatterjee joined in February 1922 the School of Tropical Medicine and in November 1923 he was appointed as Assistant Professor of Chemistry.

He had an excellent health, but since last year, he showed signs of liver trouble which proved fatal. He breathed his last on 23rd June, 1941. He leaves behind 5 sons and one daughter, all minors, his widowed wife and an aged mother.

Although engaged in the investigation of plant products of pharmacological interest as his official duties he synthesised several compounds of pharmacological interest in his spare hours and some of these have found places in standard texts.

As a man, the stern qualities of his head and heart won the respect of all who came in touch with him. His sweet and genial temper, his fellow-feeling and transparent honesty attracted the attention of all who came in his contact. He had a big heart and his purse was open to destitutes and poor students. Mr. Chatterjee was a Foundation Fellow of the Society and the following joint papers were published by him in the Society's Journal.

1. Chemical examination of roots and leaves of *Saussurea Lappa*, Clarke. Part I. (1929, 6, 517).
2. Some new hydrocupreidine derivatives. Part I. (1931, 7, 257).
3. Some new hydrocupreidine derivatives. Part II. (1932, 8, 83).
4. Studies on the enzymes of the seeds of *Butea Frondosa*. Part I. Proteolytic enzymes (1939, 15, 101).
5. Studies on the enzymes of the seeds of *Butea Frondosa*. Part II. Lipolytic enzyme (1939, 15, 107).

S. G.

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MAGNETISM AND CATALYSIS. PART V. A MAGNETIC STUDY OF THE CATALYTIC DECOMPOSITION OF POTASSIUM CHLORATE BY COBALTOSIC OXIDE AND FERRO-MAGNETIC VARIETY OF FERRIC OXIDE.

By S. S. BHATNAGAR, P. L. KAPUR, ANAND SWAROOP BHATNAGAR
AND M. A. QAYYUM.

Catalytic decomposition of potassium chlorate in presence of cobaltosic oxide and ferro-magnetic variety of ferric oxide has been studied from the magnetic point of view. A mechanism of the reaction has been suggested indicating the formation of an intermediate compound with the catalysts.

Number of hypotheses, both chemical as well as mechanical, have been put forth from time to time in order to explain the mechanism of catalytic decomposition of potassium chlorate by oxides. Recently Bhatnagar and co-workers (*J. Indian Chem. Soc.*, 1940, 17, 125) investigated this reaction from the magnetic standpoint and put forth a tentative scheme suggesting the formation of an intermediate complex of manganese. In the present investigation the authors have extended that work to the study of the catalytic decomposition of potassium chlorate in the presence of other oxides, viz., cobaltosic oxide (Co_2O_3) and ferro-magnetic variety of ferric oxide, from the magnetic standpoint.

EXPERIMENTAL.

The susceptibility values were determined on a modified form of Guoy's magnetic balance and the calculation of χ was made according to the equation,

$$\chi_{d_2} = \frac{I}{md_2} \left[(\chi_{d_1} \cdot md_1 - \chi_a \cdot m_a d_1) \frac{wd_2}{wd_1} + \chi_a m_a d_2 \right]$$

where χ_{d_1} and χ_{d_2} are respectively the specific susceptibilities of the standard substance and of the specimen, wd_1 and wd_2 are the respective pulls; md_1 and md_2 are the respective masses and $m_a d_1$ and $m_a d_2$ are the masses of air displaced respectively by the standard substance and by the specimen.

Materials Used.

Potassium chlorate (extra pure) was recrystallised and its purity ascertained by reducing it to the chloride with sulphur dioxide and estimating the chloride by Volhard's method. Purity was found to be 99.80%. The chlorate gave a susceptibility value of -0.300×10^{-6} (International Critical Tables, $\chi = -0.300 \times 10^{-6}$).

Cobaltous oxide (Co_3O_4) was prepared by heating cobaltous oxalate to redness in air in a Gallen Kemp's electric furnace (Rammelsberg, *Pogg. Ann.*, 1849, 78, 93). The oxide obtained was in the form of a black powder. Its purity was ascertained by the analysis of cobalt by the electrolytic deposition method (Found: Co, 73.38. Calc. 73.43%). The observed value of the magnetic susceptibility was $+30.63 \times 10^{-6}$ at 20° . In literature, however, divergent values of susceptibility varying between 32.00×10^{-6} and 43.6×10^{-6} are reported (cf. Herroun and Wilson, *Proc. Roy. Soc.*, 1921, 88A, 204; Hansknecht, "Magnet Chemische Untersuchungen," Strassburg, 1914, p. 38; Merck and Wedekind, "Handbuch der Krystallographisch-physikalischen Chemie," Leipzig, 1930, 186, 49). The reason for this divergence will be discussed in a subsequent paper.

Ferro-magnetic variety of ferric oxide was prepared from the ordinary red variety of Fe_2O_3 which was prepared by precipitating the ferric hydroxide from ferric chloride by the addition of ammonia and further igniting the ferric hydroxide to the oxide state at 500° in an electric furnace (Found: Fe, 69.9. Calc. 70%). Pure and dry hydrogen was then passed over the red Fe_2O_3 at 500° in an electric furnace; when it transformed into Fe_3O_4 and was further oxidised gently by a slow current of dry air at 200° – 250° for 2 hours (Found: Fe, 69.88. Calc. 70.0%).

The susceptibility of an intimate mixture of potassium chlorate and the catalyst approximately in the ratio of 4 : 1, were determined after analysis. It was then heated at different temperatures (below the temperature of spontaneous ignition) for different intervals of time, its χ value determined and the products analysed at each stage.

Methods of Estimation.

Chloride and Chlorate.—The mixture was treated with water till free of chloride and chlorate and the filtrate made to a known volume. Chloride was estimated by Volhard's method and the chlorate was reduced to chloride in an aliquot portion with sulphur dioxide and the chloride estimated as above.

Cobaltous oxide was estimated by the electrolytic method and the active oxygen determined in the insoluble residue iodometrically.

Ferric oxide was estimated by precipitation as hydroxide, followed by ignition to Fe_2O_3 .

Results so obtained are set forth in Tables I and II. The values in each case represent the mean of at least three observations.

Since the composition of the mixture and the susceptibilities of its components at various stages are known, the theoretical values of χ are those arrived at on the additivity law for a mixture.

TABLE I.

Catalytic decomposition of KClO_3 with Co_3O_4 as a catalyst.

Temp. = 20° . χ of $\text{Co}_3\text{O}_4 = +30.63 \times 10^{-6}$. χ of $\text{KClO}_3 = -0.300 \times 10^{-6}$.
 χ of $\text{KCl} = -0.516 \times 10^{-6}$.

Composition of the solid residue.

Magnetic susceptibility values ($\chi \times 10^6$).

MIXTURE I.

No.	Temp.	Time.	Co_3O_4	KClO_3	KCl	Total	Found. (a)	Calc. (b)	Diff. (a-b)
1	—	—	18.25%	81.70%	0.00%	99.95%	5.332	5.346	-0.014
2	290-300°	0.5 hr.	19.13	77.54	3.22	99.89	5.320	5.609	-0.289
3	300-310°	0.5	20.98	63.21	15.66	99.85	5.857	6.157	-0.300
4	310-320°	0.5	22.44	52.51	24.88	99.83	6.282	6.588	-0.306
5	320-330°	0.5	24.12	39.81	35.92	99.85	6.782	7.084	-0.302
6	330-345°	Spontaneous.	26.30	0.00	73.68	99.98	7.676	7.696	-0.020

MIXTURE II.

1	—	—	18.25%	81.72%	0.00%	99.77%	5.334	5.346	-0.012
2	290-300°	0.5	19.13	77.55	3.20	99.88	5.321	5.609	-0.288
3	300-310°	0.5	21.00	63.18	15.70	99.88	5.848	6.148	-0.300
4	310-320°	0.5	22.60	52.27	25.01	99.88	6.332	6.637	-0.305
5	320-330°	0.5	24.13	39.80	35.92	99.85	6.784	7.084	-0.300
6	330-345°	Spontaneous.	26.33	0.00	73.67	100.0	7.672	7.687	-0.015

TABLE II.

Catalytic decomposition of KClO_3 with ferro-magnetic variety of Fe_2O_3 Temp. = 20° .

Magnetic nature of the mixture I and II is ferromagnetic.

Composition of the solid residue.

No.	Temp.	Time. hrs.	Fe_2O_3 .	KClO_3 .	KCl.	Total.	Fe_2O_3 .	KClO_3 .	KCl.	Total.
MIXTURE I.						MIXTURE II.				
1	—	—	16.1%	83.52%	0.00%	100.02%	17.23%	82.77%	0.00%	100.00%
2	255-265°	0.5	16.77	78.09	4.04	99.90	18.55	77.01	4.33	99.89
3	270-280°	0.5	18.54	70.97	10.37	99.88	19.84	69.23	10.86	99.93
4	290-300°	0.5	20.47	58.06	21.32	99.85	21.63	56.21	22.02	99.86
5	310-320°	0.5	21.83	43.11	34.92	99.86	23.03	41.08	35.73	99.84
6	320-330°	Spontaneous.	23.03	0.00	76.96	99.99	25.12	0.00	74.81	99.93

In the case of both the catalysts a separate aliquot portion of the mixture was taken and heated in a closed tube for about half an hour upto the temperature of the spontaneous decomposition of the mixture. The gases evolved in the reaction were bubbled through potassium iodide solution in order to see if any chlorine was liberated from the mixture. It was observed that not a trace of free iodine was liberated and hence no trace of chlorine was set free in the case of the catalytic decomposition of the two mixtures.

DISCUSSION.

The numerous theories which have been advanced from time to time to explain the reaction mechanism of the catalytic decomposition of potassium chlorate by oxides are either (a) mechanical or (b) chemical in nature.

The untenability of the mechanical hypothesis has been discussed (Bhatnagar and co-workers, *loc. cit.*). Psarshevshi (*Sci. Mag. Chem. Cath. Katerinoslav*, 1926, p. 165) while investigating the catalytic decomposition of potassium chlorate by oxides suggested that the adsorbed gases are ionised by the impacts of electrons on the catalysts and thereafter act upon the salt.

To explain the mechanism of the catalytic decomposition of KClO_3 by MnO_2 and Fe_2O_3 , Bhatnagar and co-workers (*loc. cit.*) put forward the view that an intermediate compound was formed. They consequently suggested a tentative scheme which explained the evolution of chlorine; formation of traces of permanganate and the formation of the complex oxides of manganese. The scheme suggested was of the nature of a cycle of changes which ultimately result in the release of MnO_2 .

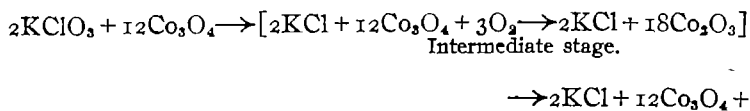
The magnetic results tabulated in Table I also conclusively show that an intermediate compound is formed in the catalysed decomposition of potassium chlorate by cobaltous oxide and the oxide takes part in the reaction. Furthermore it is clear that the observed paramagnetic susceptibility value of the reaction mixture at the intermediate stages is lower than the value calculated on the mixture law and consequently the alleged intermediate compound must be either diamagnetic or at least less paramagnetic than the original oxide.

The behaviour of catalytic decomposition of potassium chlorate by cobaltous oxide differs from the decomposition when manganese dioxide is used as a catalyst in as much as that in this case no trace of chlorine is evolved. It suggests that the reaction mechanism of catalysed decomposition by cobaltous oxide is different from that suggested for the catalysed decomposition of KClO_3 by MnO_2 .

Sodeau (*J. Chem. Soc.*, 1902, 81, 1066) in trying to explain the role of MnO_2 in the catalytic decomposition of KClO_3 suggested that there was an alternate formation and breaking up of different oxides of manganese.

The behaviour of cobaltous oxide can be similarly explained by suggesting the formation and breaking up of such oxide as Co_3O_3 , etc. The following scheme can be suggested which would readily explain the magnetic results (Table I) because pure cobaltous oxide has molecular susceptibility per metallic atom of Co as $2460 \cdot 0 \times 10^{-6}$ and pure cobaltic oxide (Co_2O_3) has molecular susceptibility value per metallic atom of Co as $2375 \cdot 0 \times 10^{-6}$ which is lower than the original Co_3O_4 . Moreover, it is known that cobaltic oxide has great tendency to change to cobaltous oxide. Therefore cobaltic oxide as soon as formed is at once changed to Co_3O_4 .

The following scheme is hence suggested :—



When the ferro-magnetic variety of ferric oxide was used as a catalyst, it was observed (Table II) that the spontaneous decomposition temperature of potassium chlorate was 330° , whereas Bhatnagar, Parkash and Singh (*loc. cit.*) observed that with the ordinary variety of ferric oxide the spontaneous decomposition temperature was 350° .

The lowering in the spontaneous decomposition temperature of KClO_3 by $\gamma\text{-Fe}_2\text{O}_3$ indicates that $\gamma\text{-Fe}_2\text{O}_3$ is a better catalyst than ordinary $\alpha\text{-Fe}_2\text{O}_3$. This inference is in accord with that of Welo and Bandisch (*Chem. Ztg.*, 1925, **49**, 961) who observed that cubic ferro-magnetic $\gamma\text{-Fe}_2\text{O}_3$ behaved as a better catalyst than trigonal variety in the oxidation of benzidine by hydrogen peroxide.

The magnetic measurements of the mixture of KClO_3 and $\gamma\text{-Fe}_2\text{O}_3$ are not given as this work is in progress.

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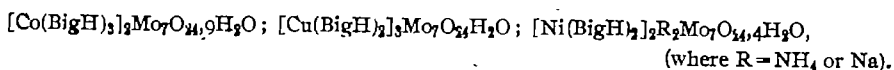
Received May 19, 1941.

ON THE COMPOSITION AND CONSTITUTION OF PARAMOLYBDATES.

BY PRIYADARANJAN RÂY AND SUSHIL KUMAR SIDDHANTA.

According to some workers the paramolybdates have the composition, $3R_2O \cdot 7MoO_3$ aq., and should be formulated as $R_6Mo_7O_{24}$ aq., while others represent them as $5R_2O \cdot 12MoO_3$ aq., or more definitely as $R_6H_8[H_2(MoO_4)_6]$ aq., due to Rosenheim. Jander in agreement with the latter view, represents the paramolybdate as $R_6[HM_6O_{21}]$ aq.

With a view to a critical examination of the problem, the following paramolybdates of complex metallic biguanide ions of high equivalent weight were prepared and their properties studied :



The results are in good accord with the older formula, $3R_2O \cdot 7MoO_3$ aq., showing that the paramolybdate ion is best represented as $[Mo_7O_{24}]^{6-}$. The conclusion is based mainly upon the analytical composition of the compounds, their dehydration, followed by rehydration, and other general chemical properties.

The composition of the paramolybdates has been a subject of long-standing controversy. One school of workers, Lotz (*Annalen*, 1854, **91**, 49), Delafontaine (*J. prakt. Chem.*, 1865, **98**, 136) and Ullik (*Annalen*, 1867, **144**, 204; 1870, **163**, 373) found the analytical values to correspond to the composition, $3R_2O \cdot 7MoO_3$ aq. ($R =$ a univalent metal atom). Later Klason assigned the composition, $5R_2O \cdot 12MoO_3$ aq., to this class of compounds (*Ber.*, 1901, **34**, 153). The ratios of Mo : R in these two formulae are fairly close, being 1.167 and 1.20 respectively; it is, therefore, difficult to ascertain which of the two formulae is correct. Junius (*Z. anorg. Chem.*, 1905, **46**, 428) on the basis of analysis of barium and thallium paramolybdates, approved of the composition, $5R_2O \cdot 12MoO_3$ aq., and this was confirmed by Wempe (*Z. anorg. Chem.*, 1912, **78**, 298) and Rosenheim (*ibid.*, 1916, **96**, 139). On the other hand, Barbieri (*Atti. R. Acad. Lincei*, 1908, **171**, 546; 1911, **201**, 18) prepared a few mixed rare earth ammonium paramolybdates to which the formula, $M(NH_4)_3Mo_7O_{24}$ aq., can be assigned ($M = La, Ce, Pr, Nd$ or Sm). Copeaux (*Compt. rend.*, 1913, **166**, 1771) suggested the constitution, $R_6[Mo(Mo_2O_7)_3O_3]$, for the paramolybdates from a study of their dehydration by heat and their absorption of ultraviolet light. Travers and Malaparade (*Bull. Soc. chim.*, 1926, **39**, 1543) from the titration values of sodium and potassium paramolybdates with alkali,

concluded that the ordinary ammonium paramolybdate constitutes mixed crystals of 10% trimolybdate with 90% Delafontaine's paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot\text{aq.}$

Jander and his co-workers (*Z. anorg. Chem.*, 1929, **180**, 129; 1930, **187**, 60; 1933, **211**, 49; 1933, **212**, 1; 1934, **217**, 65) from a detailed study of ionic diffusion in presence of an inert electrolyte, determined the masses of various polymolybdate ions, produced by the gradual addition of acids to a solution of normal molybdate. The values, thus obtained, were further supported by the results of conductometric titration of normal sodium molybdate by nitric acid, as well as by those of thermometric titration and also by a study of the absorption spectra of an increasingly acidified solution of a normal molybdate. The formula, thus suggested for the paramolybdate by Jander, is represented as $\text{Na}_5[\text{HMo}_6\text{O}_{21}]\cdot 18\text{H}_2\text{O}$, which resembles more or less closely that advocated by Rosenheim (*loc. cit.*), $\text{Na}_5\text{H}_5[\text{H}_2(\text{MoO}_4)_6]\cdot 15\cdot 5\text{H}_2\text{O}$, based on Werner's co-ordination theory.

Brintzinger and Ratanarat (*Z. anorg. Chem.*, 1935, **224**, 97) also from a measurement of the rate of electro dialysis, determined the ionic weight of polymolybdates. Their values were mostly found to be in good accord with those of Jander.

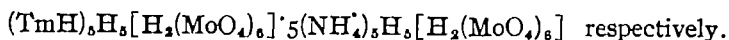
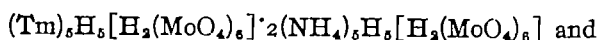
Recently Garielli and Tettamanzi (*Gazzetta*, 1935, **65**, 1009) have prepared the mixed paramolybdates of ammonium and triethanolamine and represented them by the following formulæ: (1) $(\text{TmH})(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, (2) $(\text{TmH})_2(\text{NH}_4)_4\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, (3) $(\text{TmH})_3(\text{NH}_4)_3\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, where $\text{Tm} = \text{N}(\text{C}_2\text{H}_4\text{OH})_3$, one molecule of triethanolamine. The authors showed that the compound No. 3, for instance, represented on Rosenheim's scheme, assumes the formula (c): $(\text{TmH})_3(\text{NH}_4)_3\text{H}_5[\text{H}_2(\text{MoO}_4)_6]$ with N, 4·81; NH_3 , 2·34; Mo, 39·64 per cent, in which the ratio $\text{Tm}:\text{Mo}$ becomes 0·500 and $\text{NH}_4:\text{Mo}$ as 0·333. The ratios actually found, however, approximate to 0·429 and 0·429 respectively in agreement with formula (3) assigned by them. But this is not very convincing, since the compounds can easily be represented as double salts maintaining Rosenheim's formulation. The compound (3), for instance, can be represented as:—

(a) $(\text{TmH})_3\text{H}_5[\text{H}_2(\text{MoO}_4)_6], (\text{NH}_4)_3\text{H}_5[\text{H}_2(\text{MoO}_4)_6]$, with ratio $\text{Tm}:\text{Mo} = 0\cdot 417$ and $\text{NH}_4:\text{Mo} = 0\cdot 417$, or even as (b) $(\text{TmH})_3(\text{NH}_4)_3\text{H}_5[\text{H}_2(\text{MoO}_4)_6]$, $(\text{NH}_4)_3\text{MoO}_4$ with ratio $\text{Tm}:\text{Mo} = 0\cdot 429$ and $\text{NH}_4:\text{Mo} = 0\cdot 429$. These ratios are either identical or very close to those actually found. Besides, there is no difference between the percentage values for formulæ (3) and (b) the values found by the authors are such as does not permit a definite choice between (3) and (a). This is evident from the following figures: Formulæ (3) and (b): N, 5·15; NH_3 , 3·12; Mo, 41·16 per cent. Formula (a):

N, 5'05; NH_3 , 3'06; Mo, 41'53 per cent. Expt. values (authors') : N, 5'21; NH_3 , 2'90, 3'24; Mo, 40'79, 41'22 per cent.

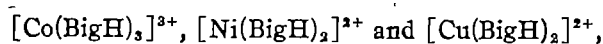
It might also be pointed out that the methods of preparing the compounds by the addition of a base is likely to raise the p_{H} value of the solution leading to the formation of normal molybdate which then combines to a double salt as in (b).

The formulae of (2) and (1) may similarly be represented as



Sturdivant (*J. Amer. Chem. Soc.*, 1937, **59**, 630) from X-ray measurements has determined the molecular weight of ammonium paramolybdate which is found to agree with the formula $(\text{NH}_4)_5\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and not with $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{MoO}_4)_6]$, suggested by Rosenheim.

It was expected that the paramolybdates of polyvalent complex cations of large ionic weight like those of



(BigH stands for a molecule of biguanide, $\text{C}_2\text{N}_3\text{H}_7$).

prepared and studied, might throw some light on this vexed problem. Experiments with this end in view have led to the isolation of mixed paramolybdates of the type $[\text{Ni}(\text{BigH})_2]_2 \text{R}_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, where $\text{R} = \text{Na}$ or NH_4 , and the pure complex paramolybdates of $[\text{Co}(\text{BigH})_3]^{3+}$ and $[\text{Cu}(\text{BigH})_2]^{2+}$.

The theoretical percentage of the constituent elements in the above four paramolybdates as required by the older formula, Rosenheim's formula and Jander's formula are summarised in Table I along with the analytical results.

An examination of Table I would show that the analytical composition of all the compounds described therein, particularly those of the mixed paramolybdates, correspond more closely to the older formula, $\text{R}_5\text{Mo}_7\text{O}_{24}\text{aq.}$, than to Rosenheim's formula, $\text{R}_5\text{H}_5[\text{H}_2(\text{MoO}_4)_6] \cdot \text{aq.}$ or Jander's formula, $\text{R}_5[\text{HMo}_6\text{O}_{21}] \cdot \text{aq.}$ It might, of course, be suggested that the mixed paramolybdates can as well be represented as double salts on the basis of Rosenheim's formula, so as to correspond approximately to the analytical results, as shown below :

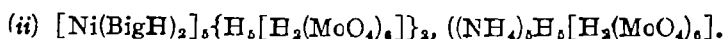
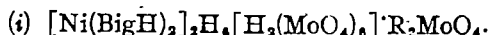


TABLE I.

Compounds.	Represented on the older formula.	Represented on the Rosenheim's formula.	As double salt with Rosenheim's or Jander's formula.	Analytical results found.
1. Cobaltic tris-bignanide paramolybdate (hydrous) (A)	$[\text{Co}(\text{BigH})_3]_3\text{Mo}_7\text{O}_{24} \cdot 9\text{H}_2\text{O}$ requires:— N, 21.64; Co, 6.07; Mo, 34.61; H_2O , 8.34%.	$[\text{Co}(\text{BigH})_3]_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— N, 21.10; Co, 5.92; Mo, 34.69; H_2O , 8.42%. Or, $[\text{Co}(\text{BigH})_3]_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— N, 21.48; Co, 6.03; Mo, 35.34; H_2O , 8.67%.	$[\text{Co}(\text{BigH})_3]_3[\text{H}(\text{HMoO}_4)_3\text{O}_4]$ requires:— N, 21.48; Co, 6.03; Mo, 35.34; H_2O , 8.66%.	N, 21.52, 21.48; Co, 6.10, 6.05, 6.10; Mo, 34.53, 34.57, 34.70, 34.64, 34.70; H_2O , 8.28, 8.25, 8.48, 8.19%.
2. Cobaltic tris-bignanide paramolybdate (anhydrous).	$[\text{Co}(\text{BigH})_3]_3\text{Mo}_7\text{O}_{24}$ requires:— Mo, 37.76%	$[\text{Co}(\text{BigH})_3]_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— Mo, 36.68%.	$[\text{Co}(\text{BigH})_3]_3[\text{H}(\text{HMoO}_4)_3\text{O}_4]$ requires:— Mo, 38.00%.	Mo, 37.67%.
3. Nickel bignanide ammonium paramolybdate.	$[\text{Ni}(\text{BigH})_3]_3(\text{NH}_4)_3\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ requires:— N, 18.28; Ni, 6.97; Mo, 39.88; NiO + MoO_3 , 68.66%.	$[\text{Ni}(\text{BigH})_3]_3(\text{NH}_4)_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— N, 19.52; Ni, 7.80; Mo, 38.25; NiO + MoO_3 , 67.25%.	$[\text{Ni}(\text{BigH})_3]_3(\text{NH}_4)_3[\text{H}(\text{HMoO}_4)_3\text{O}_4]$ requires:— N, 19.52; Ni, 7.80; Mo, 38.25; NiO + MoO_3 , 67.25%.	N, 18.39; Ni, 7.03, 7.0; Mo, 39.77; NiO + MoO_3 , 68.60%.
4. Nickel bignanide sodium paramolybdate.	$[\text{Ni}(\text{BigH})_3]_3\text{Na}_3\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ requires:— Ni, 6.93; Mo, 39.65; Na, 2.71%.	$[\text{Ni}(\text{BigH})_3]_3\text{Na}_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— Ni, 7.77; Mo, 38.12; Na, 1.52%.	$[\text{Ni}(\text{BigH})_3]_3\text{Na}_3[\text{H}(\text{HMoO}_4)_3\text{O}_4]$ requires:— Ni, 7.77; Mo, 38.12; Na, 1.52%.	Ni, 6.92; Mo, 39.41; Na, 2.64%.
5. Copper bignanide paramolybdate	$[\text{Cu}(\text{BigH})_3]_3\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ requires:— N, 21.83; Cu, 9.93; Mo, 34.91; CuO + MoO_3 , 64.77%.	$[\text{Cu}(\text{BigH})_3]_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5\text{H}_2\text{O}]$ requires:— N, 21.47; Cu, 9.74; Mo, 35.31; CuO + MoO_3 , 64.51%.	$[\text{Cu}(\text{BigH})_3]_3[\text{H}(\text{HMoO}_4)_3\text{O}_4]$ requires:— N, 21.47; Cu, 9.74; Mo, 35.31; CuO + MoO_3 , 64.51%.	N, 21.63; Cu, 9.95; Mo, 34.87; CuO + MoO_3 , 64.63%.

D(R) = Double salt with Rosenheim's formula —
 $[\text{Ni}(\text{BigH})_3]_3[\text{H}_3(\text{H}_2\text{MoO}_4)_5]_2 \cdot \text{R}_3\text{H}_3[\text{H}_2(\text{MoO}_4)_5]$.

D(J) = Double salt with Jander's formula:—
 $[\text{Ni}(\text{BigH})_3]_3[\text{H}(\text{HMoO}_4)_3\text{O}_4] \cdot \text{R}_3[\text{H}(\text{HMoO}_4)_3] \cdot 9\text{H}_2\text{O}$

where R = NH_4 or Na.

The representation (i) is untenable as there is no reason why a normal molybdate should be formed in the mixture. Nothing very definitely can be stated against the representation (ii) simply from analytical results, though there is still appreciable difference in the percentage values of Ni, Mo and specially of nitrogen. The nickel biguanide paramolybdate has been obtained in a rather impure state by adding a dilute solution of ammonium paramolybdate, drop by drop, to that of an excess of concentrated solution of nickel biguanide hydrochloride.

On the basis of Rosenheim's scheme of representation, the paramolybdates contain 3.5 molecules of "water of constitution" for every 6 Mo-atoms or 4 molecules for every 7 Mo-atoms. According to the older formula, on the other hand, all the water molecules should behave as "water of crystallisation."

Table II summarises the results of dehydration of the metal biguanide paramolybdates discussed above, before any decomposition sets in, and also of the rehydration of the dehydrated products on keeping the latter exposed to air at the room temperature.

The cobaltic *tris*biguanide paramolybdate thus loses $7\text{H}_2\text{O}$, i.e., 6.4% of its weight even at 80° ; on the basis of Rosenheim's formula, $[\text{Co}(\text{BigH})_3]_5/3\text{H}_6[\text{H}_2(\text{MoO}_4)_6]$, $5\text{H}_2\text{O}$, it should have lost only 5.42% of its weight by the removal of all its water of crystallisation ($5\text{H}_2\text{O}$) without decomposition. Besides, the loss of all the water molecules from the compound at 110° without decomposition definitely invalidates Rosenheim's representation. Table II also shows that the compound regains at the ordinary temperature the whole of its water lost during heating without any change of its original properties.

For the same reason the compounds 2, 3, and 4 in Table II should not have lost any water at 70° without decomposition according to Rosenheim's scheme; all these compounds, however, lose a part of their water at this temperature, and regain it back on subsequent exposure to air at the room temperature. No positive evidence regarding their decomposition on dehydration could, however, be obtained.

The dehydration experiments alone cannot, however, rule out Jander's formula for paramolybdates, but when coupled with the analytical results as given above, they furnish evidences against the validity of the latter.

From the considerations set forth above, it may be concluded that the composition of the paramolybdate ion is best represented by $(\text{Mo}_6\text{O}_{24})^{6-}$, as assumed in the older formula.

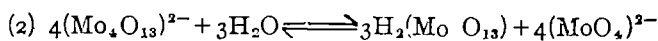
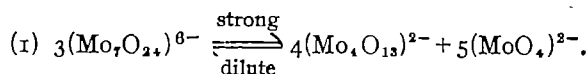
TABLE II.

Compounds	Loss of H ₂ O in mol. at					H ₂ O regained
	60°.	70°.	80°.	100°.	110°.	
1. Cobaltic trisbiguanide paramolybdate [Co (BigH) ₃] ₂ Mo ₇ O ₂₄ ·9H ₂ O	3·75	4·75	7·0	8·0	9·0	9·0 mol.
2. Nickel biguanide ammonium paramolybdate [Ni (BigH) ₂] ₂ (NH ₄) ₂ ·Mo ₇ O ₂₄ ·4H ₂ O	1·0	1·63	1·63	1·63	...	1·60
3. Nickel biguanide sodium paramolybdate [Ni (BigH) ₂] ₂ Na ₂ Mo ₇ O ₂₄ ·4H ₂ O	...	1·75	1·75	1·75	1·75	1·75
4. Copper biguanide paramolybdate [Cu (BigH) ₂] ₂ Mo ₇ O ₂₄ ·4H ₂ O	...	2·11	2·50	3·0	3·0	3·0

The Constitution and the Structure of Paramolybdate Ion.

Copeaux (*Compt. rend.*, 1913, 156, 1771), as the result of several dehydration experiments and a study of light absorption in ultraviolet region, concluded that the paramolybdates should be formulated as $R_6[Mo(Mo_2O_7)_3O_3] \cdot aq$.

Travers and Malaparade (*Bull. Soc. chim.*, 1926, 39, 1543), however, from a study of the colour reactions with potassium ferrocyanide assumed that the paramolybdate ion, $(Mo_7O_{24})^{6-}$, dissociates in solution to give the metamolybdate and the normal molybdate ions with the establishment of the following equilibrium, the relative proportion of each depending on the concentration of the solution as shown below :



↓
[gives colour reaction with ferrocyanide].

According to these authors the metamolybdate ion is represented by $(Mo_4O_{13})^{2-}$.

It has, however, been observed that both cobaltic biguanide metamolybdate and cobaltic biguanide paramolybdate are almost equally insoluble in water, while cobaltic biguanide normal molybdate is quite soluble. If any equilibrium like (1) and (2) existed in solutions of paramolybdates,

one could have scarcely expected to obtain, by adding cobaltic biguanide chloride or hydroxide to a concentrated solution of ammonium paramolybdate, a pure cobaltic biguanide paramolybdate as a precipitate without any contamination with metamolybdate, as the latter ion is supposed to abound in concentrated solutions of paramolybdate. But, as a matter of fact, pure cobaltic biguanide paramolybdate has been obtained both from the strong and dilute solutions of ammonium paramolybdate. The paramolybdate ion should, therefore, be regarded as a discrete entity by itself without any dissociation into the meta and normal molybdate ions in aqueous solution, as suggested by the above mentioned authors.

A consideration of the ionic radius ratio of Mo^{6+} and O^{2-} ions on the basis of Goldschmidt's view (*Trans. Faraday Soc.*, 1929, **29**, 253) by Pauling (*J. Amer. Chem. Soc.*, 1929, **51**, 2868) and Keggin (*Proc. Roy. Soc.*, 1934, **A144**, 75), and a study by X-ray measurement of heteropoly acids by Illingworth and Keggin (*J. Chem. Soc.*, 1935, 575) as well as by others have led to the conclusion that the polymolybdate ion in general is made up of (MoO_6) -octahedral units by sharing corners or edges. It has, indeed, been suggested by Anderson (*Nature*, 1937, **140**, 850) that in the paramolybdate ion, $(\text{Mo}_7\text{O}_{24})^{6-}$, there are six MoO_6 -octahedra linked together in a hexagonal annulus, each sharing two corners with the neighbouring octahedra and the central cavity is filled up by the remaining Mo atom with the same six-fold octahedral co-ordination with the surrounding O-atoms (*cf.* also Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", G. Routledge and Sons, Ltd., p. 194). However, this structure does not satisfy the electrostatic valency principle of Pauling (*J. Amer. Chem. Soc.*, 1929, **51**, 1010) and should be regarded as rather speculative. For the present we should, therefore, remain satisfied with the simple chemical representation of the paramolybdate ion as a Werner complex of the type $[\text{Mo}(\text{MoO}_4)_6]^{6-}$ without attempting any detailed geometrical arrangement.

EXPERIMENTAL.

Cobaltic trisBiguanidinium Paramolybdate (A).—A dilute solution (3 g. in 200 c.c.) of cobaltic trisbiguanidinium chloride (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, **16**, 621) was added, drop by drop with stirring, to a concentrated solution (5 g. in 30 c.c.) of ammonium paramolybdate. A dull red precipitate separated at once even by the addition of the first drop of the complex hydrochloride solution. The mixture was heated at 80° - 90° on the water-bath for a few minutes. The precipitate was then filtered hot,

washed several times first with hot water and then with alcohol. The product was dried in air.

The ammonium paramolybdate, used in this experiment, was obtained by recrystallising Merck's extra pure product from slightly ammoniacal solution. [Found: Mo, 54.39. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ requires Mo, 54.36 per cent].

The same compound was also prepared by adding a dilute solution (2.5 g. in 300 c.c.) of ammonium paramolybdate, drop by drop with stirring, to an excess of complex cobaltic salt solution (2 g. in 15 c.c.).

The substance formed dull red microcrystalline powder, insoluble in water or alcohol, but readily soluble in acids or ammonia.

For analysis and composition see Table I.

Dehydration.

Weight of the substance = 2.6405 g.

Temp	60°	70°	80°	100°	110°
Loss of wt. (g.)	0.0917	0.1172	0.1690	0.1934	0.2190
Loss of H_2O (mol)	3.75	4.79	6.91	7.91	8.95

H_2O (total) = 8.28% of the hydrated compound.

The whole of this water was regained after some days on keeping the dehydrated product exposed to air at the room temperature.

On adding cobaltic biguanide chloride solution to that of a normal sodium molybdate no precipitate was obtained. This shows that the cobaltic biguanide normal molybdate is soluble. The solubility of the cobaltic biguanide paramolybdate in ammonia or an excess of cobaltic biguanide hydroxide solution is evidently due to the formation of this soluble normal molybdate under the influence of alkali. The same compound could be obtained even by adding an 1% solution of cobaltic biguanide dihydrate (Rây and Dutt, *loc. cit.*), drop by drop with stirring, to a concentrated solution of ammonium paramolybdate at 50°-60°.

Nickel Biguanide Ammonium Paramolybdate (B).—A dilute solution (2 g. in 250 c.c.) of nickel biguanide hydrochloride (Rây and Purakayastha, *J. Indian Chem. Soc.*, 1941, 18, 217) was added, drop by drop with stirring, to a concentrated solution (3 g. in 20 c.c.) of ammonium paramolybdate. An immediate precipitation occurred. The mixture was heated on the water-bath for a few minutes, filtered hot and was washed several times first with hot water and then with alcohol. The precipitate was finally dried in air.

The substance forms a yellow microcrystalline powder, sparingly soluble in cold water and insoluble in alcohol. On boiling with sodium carbonate solution it liberated ammonia.

For analysis and composition see Table I.

Dehydration.

Weight of the substance = 0.9793 g.

Temp.	...	60°	70°	80°	100°
Loss of H ₂ O (g.)	...	0.0096	0.0166	0.0167	0.0170
Loss of H ₂ O (mol.)	...	0.92	1.63	1.63	1.63

The whole of water lost by heating was regained on keeping the product at the room temperature, exposed to air for some days.

Nickel Biguanide Paramolybdate.—On adding a dilute solution of ammonium paramolybdate to a concentrated solution of nickel biguanide hydrochloride a yellow microcrystalline precipitate was obtained, which, on analysis, proved to be nickel biguanide paramolybdate in a rather impure state. {Found: Ni, 9.29, 9.34; Mo, 32.99, 33.0. [Ni (BigH₂)₃Mo₇O₂₄·4H₂O requires Ni, 9.25; Mo, 35.10 per cent}. On shaking with an excess of ammonium paramolybdate solution for a long time it tends to change into the above described mixed salt.

Nickel Biguanide Sodium Paramolybdate (C).—The substance separated immediately as a yellow precipitate by adding, drop by drop with stirring, a dilute solution (1 g. in 200 c.c.) of nickel biguanide hydrochloride to a concentrated solution (3 g. in 15 c.c.) of sodium paramolybdate at 60°–70°. The mixture was kept on the water-bath for some time. The precipitate was then filtered hot, washed and dried as in the previous case.

Sodium paramolybdate was obtained by dissolving 1 mol. of MoO₃ (27 g.) in a solution containing 1 mol. of NaOH (7.5 g.); the solution was evaporated on the water-bath to a small volume, when sodium paramolybdate crystallised out on keeping. (Found: Mo, 46.35. Calc. for Na₈Mo₇O₂₄·14H₂O: Mo, 46.46 per cent).

For analysis and composition see Table I.

Dehydration.

Weight of the substance = 1.1323 g.

Temp.	...	70°	80°	100°	110°
Loss of H ₂ O (g.)	...	0.0204	0.0204	0.0211	0.0212
Loss of H ₂ O (mol.)	...	1.7	1.7	1.76	1.76

The product on exposure to air at the room temperature for some days regained its original weight.

Copper Biguanide Paramolybdate (D).—A solution (2.3 g. in 200 c.c.) of copper biguanide hydrochloride (Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617) was added, drop by drop with stirring, to a solution (2.6 g. in 20 c.c.) of ammonium paramolybdate. The mixture with the precipitate was then heated on the water-bath, filtered, washed and dried as already described. The substance forms a violet-red powder, sparingly soluble in hot water. For analysis and composition see Table I.

Dehydration.

Weight of the substance = 2.2123 g.

Temp.	.. 70°	80°	100°	110°
Loss of H ₂ O (g.)	... 0.0437	0.0535	0.0627	0.0629
Loss of H ₂ O (mol.)	... 2.11	2.59	3.04	3.04

The whole of the water, lost by heating, was regained on keeping the product exposed to air at the room temperature for some days.

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Received April 18, 1941

STUDIES IN ENZYMES. AMYLASE FROM KASERU (*SCIRPUS GROSSUS*, LINN.)

By J. P. SHUKLA.

The amylase from Kaseru has an optimum p_H between 5.8 and 6.2 and optimum temperature between 50 and 55° using buffers according to Clark and Lubbs.

This investigation relates to the presence of amylase in the tuberous root of the herb Kaseru (*Scirpus grossus*, Linn, N.O. *cyperaceæ*) its extraction and study of optimum temperature and p_H . The amylase isolated has an optimum p_H between 5.8 and 6.2 and optimum temperature between 50° and 55° in phosphate buffers.

Scirpus grossus, Linn., called *Kaseruk* in Sanskrit, *Kaseru* in Hindustani, *Kesur* in Bengali, *Kasia* in Marathi and *Gundatungagaddi* in Telegu, is a very large annual aquatic herb common throughout India. The tuberous root of the herb is found in the tanks and is about the size of a nutmeg. It is of black colour externally and is commonly used as a delicate article of food. With milk it forms a suitable nourishment in diarrhoea and vomiting (*vide* Kirtikar and Basu, "Indian Medicinal Plants," p. 1358). Analysis of tubers according to Dymock ("Pharmacographica Indica," Vol. III, Part VI, p. 555) is as follows:—

Fat, 0.65% ; sugar, 1.64% ; gum and carbohydrate, 5.69%, albuminous matter, 8.68% ; starch, 66.24% ; fibre, 4.51% ; ash, 2.06% ; moisture, 10.53 ; alkaloid, traces and nitrogen, 1.39%. The presence of amylase is not mentioned.

EXPERIMENTAL.

Preparation of the Enzyme.—A fresh supply of *Kaseru* was obtained from the Cawnpore market and its skin removed. A portion of the fruit was dried in the shade and finely powdered and another portion of the fresh fruits was crushed to extract out the juice. It was found that both the powdered starch as well as the juice showed amylolytic activity. Both can be preserved (the latter at a temperature of 4° under toluene) for a period of six months and still retain the amylolytic activity.

The juice obtained (5 c.c.) by crushing the fresh fruits was allowed to react with 2% soluble starch solution at 37° for 1 hour. Dried and powdered fruit (25 g.) was digested at 37° with 500 c.c. of water for 5 hours with occasional shaking. The clear filtrate (1 c.c.) was taken and

allowed to react with 2% starch solution (100 c.c.) at 37° for 1 hour. Also 25 g. of the dried and powdered material were triturated with dry, washed neutral sand in 500 c.c. of water for 5 hours and 1 c.c. of clear filtrate allowed to react with 100 c.c. of 2% starch solution at 37° for 1 hour. In all the three cases the action of the enzyme was stopped by pouring in an excess of Fehling's solution and boiling the reaction flasks to precipitate the copper oxide. It was filtered and estimated using Bertrand's method (Plimmer, "Practical Organic and Biochemistry", p. 228).

Treatment	Amount of CuO
Extracted juice (5 c.c.)	0.16 mg.
Dried fruit (25 g.) + 500 c.c. water digested as such (1 c.c.)	0.06
Dried fruit (25 g.) + 500 c.c. water + sand triturated (1 c.c.)	0.15

The results obtained point out the presence of amylase in the fruit. The enzyme comes out in the juice pressed out in fresh condition in fairly large proportions. It can also be preserved in the starch obtained by crushing dried fruits. Extraction of the enzyme from the starch is facilitated by triturating with dry sand while digesting out the same with cold water at 37°.

Separation of the Enzyme.—Powdered material (100 g.) was mixed up with 2 litres of water and 100 g. of neutral washed sand and triturated. It was left overnight at 37° with small amount of toluene to prevent fungus growth and then filtered. The enzyme was then precipitated with 2.5 times its volume of absolute alcohol and left over in the frigidare to settle. The supernatant liquid was decanted out and the precipitate washed with 50% alcohol (1:1) and ether solution and then dried in shallow petri dishes in air. The powder was carefully scraped and weighed. Yield on starch (impure enzyme) was 1.4%. The enzyme powder was preserved in a cool place and used for further experiments.

Effect of p_H on the Activity of the Amylase.—Erlenmeyer flasks containing 75 c.c. of a 2% soluble starch solution (made by dissolving Schering-Kahlbaum soluble starch to make 2%) and 20 c.c. of buffer solutions of increasing p_H were kept in an incubator adjusted to $32 \pm 0.5^\circ$. When the reaction mixture had attained the temperature, 5 c.c. of the enzyme solution prepared fresh by dissolving known amount of enzyme powder was added. Before adding, the enzyme solution was allowed to attain the same temperature by leaving it in the incubator for an hour. The reaction was arrested by adding 40 c.c. of the mixed Fehling's solution exactly after one hour. The flasks were then boiled for 5 minutes and the precipitated oxide of

copper was estimated using Bertrand's method (*loc. cit.*). Buffer solutions were prepared according to Clark and Lubbs method and the p_H of the respective buffers was verified by electrometric measurements with quinhydrone electrode.

TABLE I.

Starch = 1.5%. Enzyme = 0.05%. Time of reaction = 1 hour.
Temp. = $32 \pm 0.5^\circ$.

p_H	CuO using enzyme from fruit starch	juice.	p_H	CuO using enzyme from fruit starch.	juice ..
3.4	2.33 mg.	4.66 mg.	5.4	13.84	15.84
3.6	3.26	5.59	5.8	15.84	19.11
4.2	5.12	6.54	6.2	23.76	25.16
4.5	5.12	7.43	6.7	6.54	6.06
5.1	5.59	8.06	7.0	2.10	3.16
			Control	0.93	0.93

It may be observed that the optimum p_H lies in the region of 5.8 to 6.2. Other amylases from plants are also reported (Sjoberg, *Biochem. Z.*, 1922, **133**, 218, 294; 1923, **142**, 274; 1923, **189**, 118, to have their p_H optimum between 5 and 6. The optimum p_H of the enzyme extracted in the juice and the starch is the same.

Effect of Temperature on the Activity of Amylase.—The reactions were carried out in conical flasks containing 75 c.c. of a 2% starch solution, 20 c.c. of buffer of p_H 6.2 and at 0.05% concentration of the enzyme. The flasks were maintained at different temperatures in an air-oven regulated by a sensitive thermo-regulator to give the required temperatures.

TABLE II.

$p_H = 6.2$. Other conditions same as in Table I.

Temp.	CuO using enzyme from fruit starch.	Temp	CuO using enzyme from fruit starch.
21.5°	15.93 mg.	50.0°	35.31 mg.
31.0	16.71	55.0	38.73
37.0	21.30	60.0	33.17
40.0	25.16	65.0	28.17
45.0	30.20	70.0	10.93



The optimum temperature appears to be in the neighbourhood of 50 to 55° and the results are in harmony with the optimal temperatures for amylases obtained from other vegetable origin (Effront, *Compt. rend. Soc. biol.*, 1922, **86**, 274).

The author acknowledges his thanks to Mr. R. C. Srivastava, O. B. E., Director and Dr. H. D. Sen, Biochemist, Imperial Institute of Sugar Technology, Cawnpore for their keen interest and encouragement in the work.

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Received March 21, 1941

ON A RELATIONSHIP BETWEEN REFRACTIVE INDEX AND SURFACE TENSION.

BY R. C. TRIPATHI.

Lorentz and Lorenz equation for molecular refraction has been combined with Sugden's parachor equation. The resulting equation $\frac{n^2-1}{n^2+2} = \frac{R}{P} \gamma^{\frac{1}{2}}$ is found to be correct even when R and P are calculated from their corresponding atomic and configurational constants. This equation has been shown to be successful in calculating values of surface tensions with the knowledge of those of refractive indices and *vice versa*.

Lorentz and Lorenz derived the equation,

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = R$$

where n is the refractive index, d , the density and M , the molecular weight of a liquid and R , the molecular refraction. It was also shown that R is an additive quantity and it can be calculated by adding up the atomic refractions and refractions due to various linkages present in the molecule.

Sugden's parachor equation (J. Chem. Soc., 1924, 125, 1177)

$$P = \frac{M}{d} \gamma^{\frac{1}{2}}$$

where M is the molecular weight, d , the density and γ , the surface tension and P , a constant, which is additive in the same way as molecular refraction, is also a well known equation.

These two equations can be combined to give

$$\frac{n^2-1}{n^2+2} = \frac{R}{P} \gamma^{\frac{1}{2}}$$

Since R and P can both be calculated from atomic constants, a knowledge of surface tension can give refractive index and *vice versa*. To test this relationship $\frac{n^2-1}{n^2+2}$ and $\frac{R}{P} \gamma^{\frac{1}{2}}$ were calculated in cases of some eighty organic liquids listed below :—

Benzene, ether, chloroform, aniline, acetone, toluene, carbon tetrachloride, nitrobenzene, methyl alcohol, ethyl alcohol, formic acid, acetic acid, propionic acid, propyl alcohol, acetonitrile, acetophenone, acetyl chloride,* acetylene tetrabromide, acetylene tetrachloride, ethyl acetate, ethylaniline,* ethyl benzoate, ethyl butyrate, ethyl isobutyrate, ethylene bromide, ethylene chloride, ethyl formate, ethylidene chloride, ethyl iodide, ethyl propionate, amyl acetate, anisol, benzaldehyde, benzonitrile, benzophenone, bromobenzene, cyclohexane, *para*cymol, diethylamine, diethylketone, diethyl oxalate, di-isobutylamine, dipropylamine, furfural, ethyleneglycol, hexane, mesitylene,* methyl acetate, methyl ethyl ketone, methylaniline, methyl benzoate, *o*-bromotoluene, *n*-& isobutyric acid *n*-& isobutyl alcohol, allylamine, *iso*amyl alcohol, *iso*amylamine, formamide, normal butylamine, tertiary butylamine, capronitrile,* isobutylamine, isobutyl valerate, *ortho*-chloroaniline, chlorobenzene, methyl propionate, methyl propyl ketone, nitroethane, nitromethane, *ortho*-nitrotoluene, octane, paraldehyde, phenol, naphthaline, piperidine, propionitrile, propyl acetate, α -picolin, isocaproic acid.

Except in case of liquids marked with asterisk the agreement was quite good. Even in cases where the agreement was not so good, the difference did not exceed 3%.

In case of associated liquids also this equation is valid, which shows that both R and P are affected to the same extent by molecular association.

In Table I a few typical cases, where the agreement is good, have been listed.

TABLE I

Temp.	$\frac{n^2-1}{n^2+2}$	$\frac{R}{P} \gamma^{\frac{1}{2}}$	%Diff.	Temp.	$\frac{n^2-1}{n^2+2}$	$\frac{R}{P} \gamma^{\frac{1}{2}}$	%Diff.
Benzene.				Chloroform.			
8.5°	0.298	0.298		12.5	0.269	0.267	
12.3	0.297	0.297		18	0.267	0.265	0.7
15	0.296	0.296	0.1	22.4	0.266	0.264	
20	0.295	0.294					
Aniline.				Ethyl alcohol			
7.5	0.338	0.335		0	0.226	0.227	
16.4	0.337	0.333	1.0	6.8	0.224	0.226	
20	0.335	0.332		13.3	0.223	0.224	0.5
				30	0.220	0.221	

TABLE II.

Substance.	Temp.	$\frac{n^2-1}{n^2+2}$	$\frac{R}{P} \frac{1}{T}$	% Diff.
Toluene	... 14.7	0.294	0.292	0.7
Acetylene tetrabromide	... 20	0.355	0.354	0.3
Ethyl isobutyrate	... 17.8	0.238	0.236	0.8
Ethylene bromide	... 13.5	0.315	0.312	0.9
Ethylene chloride	... 20	0.266	0.268	0.7
Ethylidene chloride	... 20	0.251	0.250	0.4
Ethyl propionate	... 18.4	0.234	0.233	0.4
Anisol	... 21.8	0.301	0.298	1.0
Benzaldehyde	... 17.6	0.317	0.320	0.9
Benzonitrile	... 25.5	0.307	0.307	0.0
Furfural	... 20	0.307	0.307	0.0
Methyl ethyl ketone	... 15.9	0.232	0.230	0.9
Acetylene tetrachloride	... 20	0.290	0.287	1.0
Nitrobenzene	... 39	0.315	0.312	0.9
Ethyl butyrate	... 18	0.239	0.238	0.4
isoButyric acid	... 20	0.239	0.239	0.0

TABLE III.

Substance.	Temp.	$\frac{n^2-1}{n^2+2}$	$\frac{R}{P} \frac{1}{T}$	% Diff.
Carbon tetrachloride	... 20*	0.274	0.270	1.4
Acetonitrile	... 16.5	0.213	0.216	1.4
Acetophenone	... 19.6	0.311	0.306	1.6
Ethylaniline	... 20	0.321	0.315	1.8
Ethyl benzoate	... 20	0.297	0.290	2.4
Ethyl formate	... 20	0.221	0.218	1.3
Formic acid	... 20	0.225	0.222	1.3
Benzophenone	... 53.5	0.340	0.333	2.0
Bromobenzene	... 4.2	0.327	0.331	1.2
cycloHexane	... 16.6	0.257	0.261	1.5
p-Cymol	... 13.7	0.290	0.283	2.4
Di-Isobutylamine	... 19.6	0.248	0.245	1.2
Dipropylamine	... 19.5	0.245	0.242	1.2
Mesitylene	... 17.1	0.293	0.286	2.4
3-Methylaniline	... 20	0.329	0.322	2.1
Methyl benzoate	... 16.5	0.302	0.298	1.3
Ether	... 15	0.218	0.215	1.4
	... 21.3	0.216	0.213	
Methyl alcohol	... 12.6	0.205	0.208	1.6
	... 18	0.204	0.207	
	... 30	0.201	0.205	
Amyl acetate	... 20	0.243	0.240	1.2
Propionic acid	... 20	0.236	0.233	1.3

The usefulness of this equation will be evident from Table IV where the surface tensions of some liquids have been calculated from the knowledge of their refractive indices.

TABLE IV.

Substance.	Temp	n.	γ (obs)	γ (calc)	%Diff.
Acetone	... 20°	1'35931	23'09(N ₂)	23'35	1'1
Ethyl acetone	... 20	1'37257	23'60(V)	23'94	1'4
Ethyl alcohol	.. 20	1'36230	22'03(V)	21'92	0'5
Ethyl butyrate	.. 18	1'39302	24'44(A)	24'75	1'2
Ethyl iodide	.. 20	1'51307	28'10(N ₂)	28'05	0'2
Hexane	.. 14'8	1'37800	17'93(V)	18'28	1'9
Methyl acetate	20	1'36099	23'84(V)	23'88	0'2
Methyl propyl ketone	... 20'2	1'39946	25'08(V)	25'12	0'2
Octane	... 15'1	1'40070	21'32(V)	21'30	0'1
Acetylene tetrabromide	... 20	1'62772	48'00(N ₂)	48'26	0'6
Nitroethane	... 24'3	1'39007	31'08(V)	31'62	1'8
Diethyl oxalate	... 20	1'41043	32'90(A)	33'33	1'0
Methyl ethyl ketone	... 15'9	1'38071	24'24(V)	24'84	2'4
Nitromethane	.. 21'6	1'38133	35'60(N ₂)	35'38	0'5
Ethylidene chloride	... 20	1'41655	23'50(N ₂)	23'99	2'0

The percentage differences between the observed and calculated values of surface tension given in the last column of Table IV seem to be within the limits of experimental error as the values of surface tension found by various authors very often exhibit the percentage difference of the same order amongst themselves.

All the data for this paper have been taken from Landolt Börnstein Tabellen (1923 Edition).

The author is deeply indebted to Prof. B. Prasad for his kind interest and valuable suggestions during the course of this work.

OXANILIC ACID THIOAMIDE AS AN ANALYTICAL REAGENT.

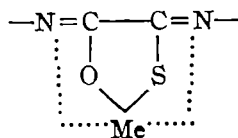
BY ANIL KUMAR MAJUMDAR.

Oxanilic acid thioamide has been used as an analytical reagent for the estimation of copper, cobalt and nickel.

Oxanilic acid thioamide, $C_6H_5NH \cdot CO \cdot CSNH_2$ may be regarded like rubeanic acid (*cf.* Rây and Ray, *J. Indian Chem. Soc.*, 1926, 3, 118) to be a compound in equilibrium with its tautomer.



It may, therefore, give rise to the inner metallic complex with copper, nickel, cobalt etc. of the type,



[Me = metal atom]

The increased weight due to the phenyl group lowers the solubility of the complex in polar solvents and the complex possesses an additional advantage of giving precipitates with nickel, cobalt and copper of definite composition which can, with the exception of that of copper, be easily washed with hot water.

The reagent behaves as a weak acid and the hydrogen atoms of the OH and SH groups are replaceable by the metals under suitable conditions. It gives characteristic coloured precipitates with most of the metals of the sulphide groups. Some of them are unstable and decompose into sulphides. As the precipitates tend to retain tenaciously the adsorbed electrolytes, it was found desirable to determine copper iodometrically, cobalt as sulphate, and nickel as oxide.

Concentration of H^+ ion exerts a great influence upon the precipitation. Copper is precipitated in presence of sodium acetate, nickel in presence of ammonia and cobalt by the sodium salt of the reagent; 2N hydrochloric acid is then added to coagulate the precipitate.

E X P E R I M E N T A L.

Preparation of the Reagent.—The thioamide was prepared from phenyl oxamide according to the method described by Reissert (*Ber.*, 1904, **37**, 3716). The reagent is soluble in alcohol, acetone, chloroform, etc. and in alkali and it melts at 176° after crystallisation from alcohol.

Detection.—The alcoholic solution of the reagent gives precipitates with a large number of cations. Mercuric mercury gives a yellow precipitate, while mercurous salts give a yellow precipitate which becomes grey on standing. Silver and lead give black precipitates. Cadmium and bismuth precipitates are yellow and brown respectively, obtained from faintly ammoniacal medium, while the zinc salt is white and antimony (trivalent) brick-red. Copper gives a violet precipitate soluble in mineral acids, in excess of ammonia, and partly in hot water. The brownish black precipitate of the cobaltous complex is soluble in mineral acids and in excess of alkali. The yellowish brown precipitate of the nickel complex shows similar properties. The copper complex is stable up to 70° , the cobalt complex up to 230° and nickel up to 160° .

Precipitation Limit for Copper, Cobalt and Nickel.—(i) One part of copper in 750,000 parts of water; using alcoholic solution of the reagent and a drop of sodium acetate solution.

(ii) One part of cobalt in 400,000 parts of water with neutral solution of the reagent followed by a drop of very dilute HCl.

(iii) One part of nickel in 2,000,000 parts of water with alcoholic solution of the reagent and a drop of dilute ammonia.

Copper Salt of the Reagent.—Copper sulphate (1 g.) and sodium acetate (4 g.) were dissolved in 1000 c.c. water and to the solution was added with stirring, a 1% alcoholic solution of the reagent in excess when copper was precipitated as a violet salt. This was filtered, washed with water and alcohol and then dried *in vacuo* over sulphuric acid. [Found: C, 37.0; H, 3.06; N, 10.7; S, 12.5; Cu, 24.4, 24.44. $(C_8H_6N_2OS) CuH_2O$ requires C, 37; H, 3.08; N, 10.8; S, 12.33; Cu, 24.47 per cent].

Estimation of Copper.—A solution of Kahlbaum's reagent quality copper sulphate was prepared and standardised by the electrolytic method. A known amount of copper solution was neutralised with dilute ammonia and then sodium acetate (2 g.) was added to the just acidic solution. The solution was then diluted to 150-160 c.c. and to it was added at room temperature, drop by drop, with stirring, a 1% alcoholic solution

of the reagent in excess. The violet copper salt was allowed to settle, and then filtered and washed with water and alcohol. The precipitate was dried and ignited to oxide. The oxide was dissolved in nitric acid and titrated iodometrically in the usual way. The results are given below.

TABLE I.

Copper			Copper		
Taken.	Found.	Error.	Taken.	Found.	Error.
0.00776 g.	0.00775	-0.00001	0.01941	0.01940	-0.000009
0.01552	0.01552	Nil	0.02190	0.02190	Nil
0.01552	0.01552	-0.00004	0.03462	0.03461	-0.00001
			0.03462	0.03460	-0.00002

Cobalt Salt of the Thioamide.—The brownish black precipitate of the cobalt complex was obtained by adding a dilute solution of the sodium salt of the reagent to a cobalt solution and then adding, drop by drop, a dilute 2*N*-hydrochloric acid to the hot solution till the precipitate just coagulated. This was filtered, washed with water and alcohol and then dried in air. [Found: N, 9.02; Co, 18.95. $(C_6H_5N_2OS)_2Co, 4H_2O$ requires N, 9.06; Co, 19.0 per cent].

Estimation of Cobalt.—A solution of Kahlbaum's reagent quality 'nickel free' cobalt chloride solution was prepared and its strength was determined by estimating as cobalt sulphate. To a solution of cobalt chloride was added an excess of sodium salt of the reagent (1 g. of the reagent per 100 c.c. solution). It was then diluted to 200 c.c. and heated to boiling. To the hot solution was then added 2*N*-hydrochloric acid, drop by drop with stirring, till the precipitate just coagulated. The brownish black precipitate was then allowed to settle, filtered hot and washed with hot water. This was then dried, ignited to oxide and then converted to anhydrous sulphate. The results are given below.

TABLE II.

C o b a l t		Cobalt sulphate.	Error.	C o b a l t		Cobalt sulphate.	Error.
Taken.	Found.			Taken.	Found.		
0.01168 g.	0.01168 g.	0.0307 g.	Nil.	0.02336	0.02338	0.0614	+0.00002
0.01168	0.01171	0.0308	+0.00003	0.028032	0.02804	0.0737	+0.000008
0.018688	0.01868	0.0491	-0.000008	0.03504	0.03504	0.0921	Nil

Nickel Salt of Thioamide.—The yellowish brown nickel compound was obtained by adding an alcoholic solution of the reagent to the solution

of a nickel salt, rendered alkaline with dilute ammonia. The solution was heated to boiling and then filtered and washed with water and alcohol. The air-dried salt was then analysed. [Found: N, 10.31; Ni, 21.49. ($C_6H_6N_2OS$) Ni, $2H_2O$ requires N, 10.26; Ni, 21.52 per cent].

Estimation of Nickel.—A solution of Kahlbaum's reagent quality nickel chloride was prepared and standardised by dimethylglyoxime method. To a solution of nickel chloride an excess of 1% alcoholic solution of the reagent was added and the mixture rendered alkaline with dilute ammonia. The solution was then diluted to 200 c.c. and heated to boiling. The precipitate was allowed to settle, filtered hot and washed with hot water. The precipitate was dried and gently ignited to oxide. The results are given below.

TABLE III.

Nickel Taken.	Nickel Found.	Ni oxide.	Error.	Nickel Taken.	Nickel Found	Ni oxide.	Error.
0.01124 g.	0.01132 g.	0.0144 g.	+0.00008	0.04496	0.04486	0.0571	-0.0001
0.02248	0.02248	0.0286	Nil	0.05620	0.05626	0.0716	+0.00006
0.03372	0.03379	0.0430	+0.00007	0.06744	0.06744	0.0858	Nil
				0.07868	0.07868	0.1001	Nil

The author's best thanks are due to Prof. P. Rây for the facilities received in conducting this piece of work in his laboratory.

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Received May 25, 1941.

QUINOLINE-8-CARBOXYLIC ACID AS AN ANALYTICAL REAGENT. PART I.

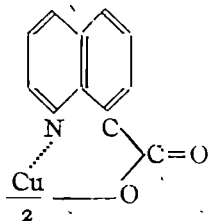
ANIL KUMAR MAJUMDAR.

Quinoline-8-carboxylic acid has been used as an analytical reagent for the estimation of copper. Copper has been found to be completely precipitated in pH as low as 2.78. In neutral solution copper gives a distinct precipitate even at a dilution of 1 in 4,000,000 parts.

It was well known that reagents like anthranilic acid (Funk, *Z. anal. Chem.*, 1933, **91**, 332; 1934, **96**, 385; 1933, **98**, 241), α -quinaldinic acid (Ray and Bose, *ibid.*, 1933, **96**, 400), 8-oxyquinoline (Berg, *ibid.*, 1927, **70**, 341) gave insoluble inner metallic complexes with some metals and thus enable the estimations and separations of metals from each other to be made under specified conditions.

8-Oxyquinoline and α -quinaldinic acids form five membered rings with the metal atoms, whereas quinoline-8-carboxylic acid, like anthranilic acid is found to form a six membered ring complex with the metal atom. Like α -quinaldinic acid this quinoline-8-carboxylic acid was found to give complete precipitation with copper, cadmium as also a red colouration with ferrous iron.

In the literature (Skraup, *Monatsh*, 1900, **2**, 532) copper compound of the reagent was described as hydrated needles. It was found that this copper compound lost all its water at 150° . The metal complex of the acid can be represented as follows:



The copper compound is appreciably soluble in mineral acids, acetic acid and in ammonia.

EXPERIMENTAL.

Preparation of Quinoline-8-carboxylic Acid.—The acid was obtained by the oxidation of 8-methylquinoline with chromic acid. The base was

prepared according to the method described by Knuppel (*Ber.*, 1896, 29, 705). The acid is appreciably soluble in cold water, more so in hot water and alcohol; very soluble in acids and in alkali solutions; m.p. 187° after crystallisation from water.

Salts of Quinoline-8-carboxylic Acid.—Copper, silver and calcium salts of the acid have been described in the literature. The copper salt of the composition $\text{Cu}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2$ forms insoluble, light blue, hydrous needles. The calcium salt $2\text{Ca}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 + \text{C}_{10}\text{H}_7\text{O}_2\text{N}$ is remarkably soluble in water and silver salt $\text{Ag}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})$ is very difficultly soluble in water. The reagent has also been found to give a white insoluble cadmium, lead, mercuric and thalious salt and a red colouration with ferrous salts. These are soluble in strong mineral acids.

Copper Salt of Quinoline-8-carboxylic Acid.—The light blue copper salt was prepared by the addition of the sodium salt of the reagent to a solution of sulphate, slightly acidified with a decinormal solution of sulphuric acid. The copper compound was filtered and washed by decantation with cold water at room temperature and then dried at 150°. The salt on analysis gave [Found: Cu, 15.59; N, 6.9. Calc. for $2\text{Cu}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2$: Cu, 15.597; N, 6.87 per cent].

The copper salt was found to be slightly soluble also in hot water, and melts with decomposition at about 288°.

Detection and Estimation of Copper.—In neutral solution copper gives a distinct precipitate even at a dilution of 1 in 4,000,000 parts.

A solution of copper sulphate prepared from electrolytic copper was standardised electrolytically. A measured quantity of this solution was neutralised with dilute ammonia and an excess of decinormal sulphuric acid (2-14 c.c.) was added. The solution was diluted to 150-180 c.c. and then to the cold solutions or to the solution at room temperature was added an excess of sodium salt of the acid (1 g. of quinoline-8-carboxylic acid per 100 c.c. solution) drop by drop with constant stirring, when a light blue precipitate of copper was formed. This was then allowed to settle, filtered through a porcelain gooch crucible and washed with cold water. The copper precipitate must be well washed with water otherwise the results tend to be too high due to the adsorption of electrolytes. The copper salt was then dried at 150° and weighed. The amount of copper was calculated from the formula $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Cu}$. The p_{H} of the filtrate from the copper precipitation was determined in each case by the quinhydrone electrode. The results are given in Table I. In Table II are given results due to the precipitation of copper in presence of free acetic acid and in Table III are

QUINOLINE-8-CARBOXYLIC ACID AS AN ANALYTICAL REAGENT 421

given results in presence of acetic acid and sodium acetate or excess of sodium salt of the reagent.

TABLE I.

p_H Range over which copper was completely precipitated.

No.	N/10-H ₂ SO ₄ .	Reagent.	Total.	Wt. of vol. Cu ppt.	Copper		p _H	Error.
					present.	found.		
1	2 ml	20ml. 180ml.	0.1129 g.	0.01759 g.	0.01760 g.	6.9	+0.000008	
2	2	20 180	0.1128	0.01759	0.01758	7.0	-0.000001	
3	4	17 180	0.1130	0.01759	0.01762	6.3	+0.000028	
4	4	17 180	0.1132	0.01759	0.01765	6.3	+0.000058	
5	6	20 180	0.1134	0.01759	0.01768	3.4	+0.000088	
6	6	20 180	0.1131	0.01759	0.01763	3.4	+0.000038	
7	6	17 180	0.1130	0.01759	0.01762	3.02	+0.000028	
8	6	17 180	0.1128	0.01759	0.01758	3.02	-0.000001	
9	7	17 180	0.1128	0.01759	0.01758	2.78	-0.000001	
10	7	17 180	0.1132	0.01759	0.01765	2.78	+0.000058	
11	2	10 150	0.0614	0.00953	0.00957	3.19	+0.000037	
12	2	10 180	0.0612	0.00953	0.00954	3.32	+0.000006	
13	4	20 150	0.1223	0.01907	0.01906	3.7	-0.000001	
14	4	20 150	0.1224	0.01907	0.01908	3.8	+0.000001	
15	8	30 150	0.1835	0.02860	0.02861	3.13	+0.000005	
16	10	30 150	0.1836	0.02860	0.02863	2.91	+0.000025	
17	14	40 150	0.2446	0.03814	0.03814	2.93	Nil	
18	14	40 150	0.2442	0.03814	0.03807	2.82	-0.000007	

In the presence of free acetic acid it has been found that the copper salt has a solubility in free acetic acid.

TABLE II.

No	N-Acetic acid	Reagent.	Total vol	Wt. of Cu ppt.	C o p p e r		p _H .	Error.
					present.	found.		
1	8 ml	10 ml.	150 ml.	0.0593 g.	0.009535 g.	0.00924 g.	3.34	-0.00029
2	8	10	150	0.0581	0.009535	0.00905	3.34	-0.000478

TABLE III.

No.	N-Acetic acid.	Reagent.	Total vol.	Wt. of Cu ppt.	Copper		p_H .	Error.
					present.	found.		
* ₁	10 ml.	10 ml.	150 ml.	0.0611 g.	0.00953 g.	0.00952 g.	4.86	-0.000012
* ₂	10	10	150	0.0610	0.00953	0.00950	4.9	-0.000027
3	8	20	150	0.0614	0.00953	0.00957	3.7	+0.000037
4	10	20	150	0.0615	0.00953	0.00958	3.62	+0.000053
5	12	20	150	0.0612	0.00953	0.00954	3.61	+0.000006

* With 2 g. of sodium acetate.

During the precipitation of copper in the presence of normal acetic acid either a few grams of sodium acetate or a large excess of sodium salt of the reagent must be added to obtain good results.

That the solubility in acetic acid has got nothing to do with the p_H of the solution can be very well judged from the results. In the presence of mineral acid at a lower p_H value, the copper is completely precipitated, whereas in free acetic acid at a higher p_H value the copper is incompletely precipitated.

Further work in this line is in progress.

The author's best thanks are due to Prof. P. Rây for the facilities received in conducting this piece of work in his laboratory.

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Received May 20, 1941.

STUDIES OF SOME PHYSICAL FACTORS IN THE ELECTRO-DEPOSITION OF NICKEL ON IRON.

BY DUSHYANT NARASINGASA SOLANKI AND DAMRI SINGH.

Results are given for the optimum conditions for the production of a smooth, bright and adherent deposit of nickel on iron from a bath containing nickel sulphate, nickel chloride and boric acid. Data are given for the cathode efficiency in respect of nickel deposition under the influence of the electrolyte concentration, the current density, the duration, the inter-electrode distance, the temperature, the agitation of the bath, the superposition of A.C., and that of the addition of a large number of organic and inorganic agents in different proportions, such as aluminium sulphate, chromic acid, cadmium chloride, hydrogen peroxide, gelatine etc. The possible role of the addition agents is also discussed.

Detailed measurements are made of the cathode efficiency of nickel in the presence of methyl and ethyl alcohol, glycerol, mannitol and sucrose whose proportions were varied over a wide range. Data are also given for conductivity, relative viscosity and density.

Introduction by Adams in 1866 of aqueous nickel ammonium sulphate for the nickel bath was soon followed by important advances in the technique of the metal deposition and the diversity of its applications. The value of the nickel coat is chiefly due to (i) the brilliant lustre on polishing, (ii) its durability in contact with the atmosphere, suffering little tarnishing, and (iii) hardness and mechanical strength. The use of the above bath material had, however, suffered from considerable drawback, as thick and coherent deposits could not be procured. This was attributed to the use of ammonia by Madsen (*Trans. Amer. Electrochem. Soc.*, 1921, 39, 483). This view was confirmed by Foerster (*Z. Elektrochem.*, 1897, 4, 160). Thick lustrous and adherent deposits of nickel were obtained by using (a) nickel sulphate or nickel chloride (*cf.* Foerster, *loc. cit.*; Karl Engemann, *ibid.*, 1911, 17, 910), (b) a single salt of nickel (*cf.* Merrick, *Chem. News*, 1910, 26, 209) and (c) a single salt of nickel in the presence of an ammonium salt (*cf.* Fischer, *Z. Elektrochem.*, 1907, 13, 361). Very satisfactory results were also obtained from a solution containing nickel ammonium sulphate and a conducting salt like ammonium chloride or nickel chloride (*cf.* Kasyer, *Chem. Zentr.*, 1878, 127; Bennet, Kenny and Dugliss, *J. Phys. Chem.*, 1914, 18, 373). Riedel (*Z. Elektrochem.*, 1915, 21, 5; 1916, 22, 281) studied the electrodeposition of nickel from the chloride solution containing free HCl and CH_3COOH . Kohlschuter and Vuilleumier (*ibid.*, 1918, 24, 300)

made an extensive study of the deposition of nickel from various solutions under differing conditions. Bath consisting of nickel sulphate, nickel chloride and boric acid was first suggested by Hammond (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 103); it was used with some modification by later workers (cf. Watts, *ibid.*, 1931, **59**, 193; *Month. Rev. Amer. Electroplater's Soc.*, 1931, No. 3, 4; Phillips, *Trans. Amer. Electrochem. Soc.*, 1930, **58**, 221; 1931, **59**, 393; Phillips and co-workers, *ibid.*, 1930, **58**, 207, 241; Stager, *Helv. Chim. Acta*, 1920, **3**, 584; Potter, *E.P.*, 244, 166; Gardner *U.S.P.*, 1642, 235; Eckardt, *Chem. Zentr.*, 1934, II, 3040; Arnold and co-workers, *B.P.*, 437224; Roub, *Mitt. Forsch. Inst., Edelmet Schwal Grund*, 1935) and others studied the influence of adding foreign substances as addition agents. Phillips (*Month. Rev. Amer. Electroplater's Soc.*, 1932, **19**, No. 2, 9) and Cuthbertson (*Metallurgia*, 1932, **7**, 557) concluded that addition of organic substances were of no use in a nickel bath. Isгарисhev and Rayikovitch (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 255) investigated the influence of adding a large number of inorganic salts, especially the chlorides of alkali and alkaline earth metals, to the plating bath. With the exception of the work by Harr (*Trans. Amer. Electrochem. Soc.*, 1933, **64**, 203), Essin and Alfimova (*ibid.*, 1935, **68**, 255) and of Fedoteev and Kinkulski (*Z. anorg. Chem.*, 1935, **224**, 337) but little quantitative data are available in the literature on nickel deposition under differing conditions. In the present investigation an attempt has, therefore, been made to obtain this information quantitatively in respect of the influence of several factors (*vide infra*).

EXPERIMENTAL.

The electrolysis was carried out in a small glass trough of about 200 c.c. capacity, kept immersed in a thermostat and maintained at the desired temperature. The temperature of the bath solution was controlled within $\pm 0.2^\circ$. The anode used was a thick plate of nickel (99—99.9%) of size 3.5×3 cm. A thin plate (3×3 cm. approx.) of iron serving as the cathode was first rendered free from grease by dipping it in a hot alkaline solution (43 g. Na_2CO_3 , 17 g. NaOH and 13 g. Na_3PO_4 in 1000 c.c. water) for a few minutes and then washing it with water; it was next immersed in moderately strong nitric acid to remove surface scales and rust and to loosen the coating of carbon. It was then well washed with water and was made an anode in the etching solution (100 g. H_2SO_4 and 100 g. Na_2SO_4 in 1000 c.c. water) and current was passed for 15-20 minutes. The plate was made an anode to prevent it from becoming brittle owing to the occlusion

of hydrogen evolved at the cathode. This gave an uniformly etched and smooth surface. It was next rubbed with sodium carbonate and washed with water. It was, afterwards, dipped momentarily into the 'bright dip' (5 parts by weight of 55Be-H₂SO₄ and 1 part concentrated HNO₃; 1000 c.c. of this solution containing 1.57 g. of NaCl), which imparted an additional brightness to the plate. The plate was then washed with distilled water and finally with alcohol, dried and weighed accurately. A copper coulometer was used to give the measure of the quantity of electricity passed through the electrolyte; the coulometer solution was prepared according to Ottel's recommendations (*Chem. Ztg.*, 1893, 17, 543). The current was obtained from storage cells; the circuit included an electrolytic bath, copper coulometer, a precision type ammeter and an adjustable resistance in series and voltmeter, connected across the electrodes in the bath.

Two stock solutions (A) and (B) were prepared; (A) was made by dissolving 280.7 g. of pure crystallised NiSO₄·7H₂O in 1000 c.c. water and (B) by dissolving 25 g. of NiCl₂·6H₂O and 50 g. of boric acid in 1000 c.c. water. The solutions used in the following experiments were prepared by mixing (A) and (B) in the required proportion or with the appropriate dilution or additions of the other materials used in this work. The strength of the mixed solutions, containing the same amounts, *viz.*, 12.5 and 25 g. of NiCl₂·6H₂O and H₃BO₃ respectively, per litre of the solution, is expressed, for the sake of convenience, in terms of mols per litre, of NiSO₄·7H₂O only (Tables IA & II). The *p_H* values given for the solutions used in this work are colorimetric, uncorrected. The precaution, to switch on the current before the plate (cathode) was introduced, was always observed to avoid the deposition of nickel by immersion. To investigate the optimum conditions for the production of smooth lustrous and adherent deposit of nickel the following factors were studied, over ranges as indicated:

Optimum conditions

(a) Electrolyte concentration, <i>M</i> to <i>M</i> /4 <i>M</i> /2
(b) Current density, 5 to 108 amp./sq. ft. 15 amp./sq. ft.
(c) Time, 5 to 60 minutes 30 min.
(d) Inter-electrode distance, 5 to 2 cms 3.5 cm

Measurements were made of the cathode efficiency for Ni-deposition in respect of the influence of the factors (a), (b) (Tables II and III), temperature (Table IVA, B, c), agitation of the bath and superimposition of A.C. (Table V), cathode material (Table VI), addition of (i) organic and inorganic agents (Table VII) in small quantities, *viz.*, HgCl₂, CdCl₂, SnCl₂,

$\text{Al}_2(\text{SO}_4)_3$, $18\text{H}_2\text{O}$, CrO_3 , glue, thymol, egg-albumin, dextrine, H_2O_2 , pyridine, CS_2 and acetone and of (ii) non-electrolytes (Tables VIII to XII) in larger proportions, viz., methyl and ethyl alcohol, glycerol, mannitol and sucrose. The nature of the nickel deposit produced in each of these experiments is also recorded as examined with a microscope. The cathode efficiency in any given experiment was calculated by the relation,

$$\% \text{ Cathode efficiency} = \frac{100 \times \text{equiv. wt. of Cu} \times \text{wt. of Ni deposit}}{\text{Equiv. wt. of Ni} \times \text{wt. of Cu (coulometer) deposit}}$$

To obtain further information in regard to the results obtained for the influence of methyl and ethyl alcohol, glycerol, mannitol and sucrose on the depositional behaviour of the bath solution, corresponding electrolytic conductivity was determined on a Pye's modified Post Office Box with the usual precautions (*cf.* Joshi and Solanki, *J. Indian Chem. Soc.*, 1937, **14**, 323; 1940, **17**, 627). The cell constant determined by using $\text{N}/50\text{-KCl}$ was found to be 0.3777. These results are given in column 6 of Tables VIII to XII. Relative viscosity was determined for each of the above mixtures by using Ostwald's and Scarpa's (in few cases) method at $25 \pm 0.1^\circ$ with the usual precautions (*cf.* Joshi and Solanki, *loc. cit.*). Specific gravities corresponding to these were determined at the above temperature. These results are given in columns 7 and 8 in Tables VIII to XII.

Results showing the influence on cathode efficiency of electrolyte concentration, current density and temperature are shown graphically in Fig. 1. Similarly the cathode efficiency, specific conductivity, relative viscosity and specific gravity are plotted against percentages of the non-electrolyte added by appropriate selection of the scale units in the same figure to economise space, in Figs. 2 and 3.

TABLE IA.

Variation of electrolyte concentration.

Temp. = 30° . p_{H} = 5.2–6.0. Time = 30 min. Inter-electrode distance = 5 cm. C.D. = 18 amp./sq. ft.

Electrolyte conc	Nature of deposit.
M	Good; bright and uniform deposit with fine structure.
M/2	Very good, bright and improved deposit with fine-grained structure.
M/4	Fairly bright deposit with uniform structure.

TABLE IB.

Variation of the duration of electrolysis.

Conc. = $M/2$. C.D. = 8 amp./sq. ft. Other factors same as in Table IA.

Time.	Nature of deposit.
5 min.	Very thin and dull deposit.
10	Do.
15	Improvement in the deposit.
30	Fairly good and bright deposit with fine structure.
60	Do.
120	Do.

TABLE IC.

Variation of current density.

Conc. = $M/2$. Other factors same as in Table IA.

C.D. in amp./sq. ft.	Nature of deposit.
5.0	Practically no deposition of the metal ; evolution of hydrogen at the cathode.
8.0	Fairly good and bright deposit with fine-grained structure.
15.0	Bright, lustrous and shining deposit.
20.0	Very bright and uniform deposit ; improvement in the structure
30.0	Do.
37.0	Do.
45.0	Lustre of the deposit gets diminished.
59.0	Dull and greyish black deposit showing a tendency to 'peel' off.
77.8	The deposit especially at the edges is loose, powdery and black, and gets easily washed off.
108.6	Burnt and powdery deposit all over the plate ; rapid evolution of hydrogen.

TABLE ID.

Variation of inter-electrode distance.

Conc. = $M/2$. Temp. = 30° . Time = 30 min. $p_H = 5.2-6.0$.

C.D. = 30 amp./sq. ft.

Inter-electrode distance.	Nature of deposit.
5	Fairly good and uniform deposit.
3.5	Bright and lustrous deposit with fine-grained structure
2.0	Do.

TABLE II.

Effect of concentration.

Inter-electrode distance = 3.5 cm. Time = 30-40 min.

Temp. = 25°. $p_H = 5.6$. C.D. = 12.5 amp./sq. ft.

Conc.	Ni deposit.	Cu deposit (Coulometer).	Cathode efficiency.	Conc.	Ni deposit.	Cu deposit (Coulometer).	Cathode efficiency.
M	0.0328 g.	0.0578 g	61.4	$M/8$	0.0295	0.0621	51.4
	0.0340	0.0604	61.0		0.0318	0.0665	51.8
$M/2$	0.0444	0.0828	58.1	$M/16$	0.0335	0.0748	48.5
	0.0446	0.0823	58.7		0.0336	0.0751	48.5
$M/4$	0.0304	0.0606	54.4				
	0.0385	0.0766	54.5				

TABLE III.

*Effect of current density.*Conc. = $M/2$. $p_H = 5.6$. Temp. = 25°. Inter-electrode distance = 3.5 cm.

C.D. (amp./ ² ft. deposit.)	Ni deposit. (Coulometer).	Cu deposit. (Coulometer).	Cathode efficiency.	C.D. (amp./ ² ft. deposit.)	Ni deposit. (Coulometer).	Cu deposit. (Coulometer).	Cathode efficiency.
2.5	0.0000 g.	0.0584 g.	0.0	20.0	0.0807	0.0962	90.8
					0.0807	0.0963	90.7
6.5	0.0181	0.0562	36.4	25.0	0.1153	0.1289	96.8
	0.0199	0.0590	36.5		0.1094	0.1203	96.8
	0.0272	0.0636	46.4	27.5	0.1320	0.1504	94.9
9.4	0.0277	0.0643	46.9		0.1062	0.1206	95.1
	0.0572	0.0936	66.1	37.5	0.1577	0.2346	72.3
15.0	0.0571	0.0936	66.0		0.1267	0.1916	72.1

TABLE IVA.

*Influence of temperature.*Conc. = $M/2$. $p_H = 5.6$. Time = 20-30 min. Inter-electrode distance = 3.5 cm. C.D. = 8 amp./sq. ft.

Temp.	Ni deposit.	Cu deposit.	Cathode efficiency.	Remarks.
15°	0.0121 g.	0.0422 g	31.1%	Bright deposit with granular structure.
25	0.0229	0.0603	41.6	Bright and coarse deposit
35	0.0232	0.0471	52.3	Bright, smooth and uniform deposit.
50	0.0256	0.0478	58.0	Much improvement in the structure.
70	0.0263	0.0484	58.7	Deposit gets blackened or burnt
85	0.0283	0.0518	59.2	Loose, powdery and black deposit.

TABLE IVB.

Influence of temperature.

C.D. = 15 amp./sq. ft. Other factors same as in Table IVA.

Temp	Ni deposit.	Cu deposit	Cathode efficiency.	Remarks
15°	0.0504 g.	0.0918 g.	59.5%	Bright but coarse deposit.
25	0.0572	0.0936	66.1	Do.
35	0.0638	0.0921	75.0	Much improvement in the structure.
50	0.0710	0.0932	82.5	Very bright and smooth deposit.
70	0.0608	0.0748	88.0	Deposit blackens and shows a tendency to peel off.
85	0.0516	0.0613	91.2	Loose, powdery and burnt deposit.

TABLE IVc.

Influence of temperature.

C.D. = 25 amp./sq. ft. Other factors same as in Table IVA.

Temp.	Ni deposit	Cu deposit	Cathode efficiency.	Remarks.
15°	0.0785 g.	0.1038 g	81.9%	Good and satisfactory deposit.
25	0.1094	0.1203	96.8	Very bright and shining deposit with fine-grained structure.
35	0.1346	0.1502	97.0	Do.
50	0.0907	0.0989	97.6	Deposit becomes coarse and nodular.
70	0.1088	0.1238	95.1	Dull, black and coarse deposit
85	0.1026	0.1178	94.5	Do.

TABLE V.

*Effect of agitation and superimposing A.C. on D.C.*Conc. = $M/2$. $p_H = 5.6$. Temp. = 25°. Time = 30 min.

Inter-electrode distance = 3.5 cm.

C.D. in amps./sq. ft.		Cathode efficiency.	Remarks.
15.0	Without agitation.	66.1%	Deposit bright but granular.
"	With "	63.4	Better and improved deposit with fine-grained structure.
50.0	Without agitation.	—	Dull and burnt deposit with irregular structure.
"	With "	—	Much improvement in the lustre of the deposit; irregularity of the structure gets lessened.
15.0	A.C. superimposed	20.1	A.C. was first started and then followed by D.C.
"	"	20.8	D.C. was first started and then A.C. superimposed.

TABLE VI.

Effect of the cathode material.

C.D. = 15 amp./sq. ft. Other factors same as in Table V.

Cathode material.	Ni deposit.	Cu deposit (Coulometer).	Cathode efficiency.	Remarks.
Iron	0.0572 g.	0.0932 g.	66.1%	Good, shining and granular deposit.
Cu (polished)	0.0776	0.1198	70.2	Fairly good deposit with fine structure.
	0.0709	0.1088	70.4	
Cu (plated)	0.0734	0.1141	69.6	Do.
	0.0780	0.1207	69.8	
Cd (plated)	0.0706	0.1140	68.1	Shining and granular deposit.
	0.0549	0.0872	68.1	
Ni (")	0.0736	0.1206	66.1	Very good deposit with fine structure.
	0.0662	0.1092	66.2	
Co (")	0.0698	0.1120	67.8	Do.
	0.0774	0.1232	68.1	
Hg (Cu-amalgamated)	0.0740	0.1138	70.4	Dull-white deposit.
	0.0744	0.1146	70.3	
Pb	0.0701	0.1076	70.5	Fine, regular and coherent deposit.
	0.0704	0.1080	70.6	
Sn	0.0556	0.0888	67.8	Do.
	0.0555	0.0886	67.8	
Ag (plated)	0.0662	0.1125	65.8	Amorphous deposit with pitting effect.
	0.0698	0.1156	65.8	
Au (plated)	0.0661	0.1093	66.0	Shining, crystalline and fine deposit.
	0.0631	0.1034	66.1	
Cr (plated)	0.0693	0.1090	68.8	Powdery and amorphous deposit.
	0.0671	0.1076	68.5	
Pt (smooth)	0.060	0.0984	65.7	Non-coherent deposit with pitting effect.
	0.058	0.0954	65.9	

TABLE VII.

Influence of addition agents.

C.D. = 15 amp./sq. ft. Other factors same as in Table V.

Addition agent	Amount of A). (A) in 100 c.c. soln.	Ni deposit	Cu deposit (coulometer).	Cathode efficiency.	Remarks.
Nil	0	0.0572 g.	0.0936 g	66.1%	Bright & granular deposit.
HgCl ₂	0.1 g	.	.	.	Dull & black deposit.
CdCl ₂	0.005	Good & shining deposit.
"	0.013	Do.
"	0.025	0.072	0.1050	69.1	} Much improvement in the deposit.
"	"	0.072	0.1046	69.2	
"	0.05	0.0542	0.0824	71.2	} Deposit very bright and lustrous.
"	0.05	0.0570	0.0862	71.6	
"	0.25	0.0547	0.0824	72.1	Deposit gets blackened.
SnCl ₂	0.013	No improvement.
"	0.03	Deposit dull, black and unsatisfactory.
Al ₂ (SO ₄) ₃ , 18H ₂ O	0.1	0.0564	0.0928	66.0	Deposit shining but coarse
"	0.5	0.0445	0.0766	63.0	} 63.0 Much improvement.
"	"	0.0445	0.0766	63.0	
"	1.0	0.0443	0.0744	62.0	Bright, lustrous and fine-grained deposit.
"	2.0	0.0446	0.0782	60.8	Bright but nodular deposit.
CrO ₃	0.005	0.0304	0.1082	30.4	} 30.5 Dull and black deposit with irregular structure.
"	"	0.0306	0.1088	30.7	
"	0.01	0.0210	0.1051	21.6	} 21.7 Do.
"	"	0.0218	0.1084	21.8	
"	0.02	0.0096	0.1306	7.96	} 7.95 Very thin and black deposit,
"	"	0.0096	0.1308	7.94	
"	0.025	0.0000	0.1082	0.0	} 0.0 No deposit; copious evolution of hydrogen.
"	"	0.0000	0.1084	0.0	
H ₂ O ₂ (3%)	0.025 c.c.	0.0427	0.0663	69.8	} 69.8 Shining deposit with fine structure.
"	"	0.0429	0.0666	69.8	

TABLE VII (contd.).

Addition agent (A)	Amount of (A) in 100 c.c. soln.	Ni deposit.	Cu deposit (coulometer).	Cathode efficiency.	Remarks.
H ₂ O ₂ (3%)	0.05 c.c.	0.0448 g	0.0666g. 72.9	72.9%	Shining deposit with fine structure.
		0.0448	0.0666 72.9		
"	0.10	0.0504	0.0693 78.6	78.6	Further improvement in structure.
		0.0502	0.0690 78.6		
"	0.20	0.050	0.0650 83.3	83.4	Diminution in lustre.
		0.0508	0.0662 83.5		
"	0.50	0.0506	0.064 85.6		Greyish-white deposit.
"	1.0	0.0528	0.0646 88.9		Greyish and black deposit
Pyridine	0.0025		Deposit gets spoiled
CS ₂	0.0035		Black streaks throughout the plate
Acetone	0.5				Dull and black deposit
Glyc	0.01 g	0.0384	0.0662 66.7	66.7	Bright and shining deposit with nodular structure
		0.0385	0.0664 66.7		
"	0.05	0.0546	0.0908 66.3	66.3	Do.
		0.0546	0.0908 66.3		
"	0.1	0.0512	0.0781 66.0	66.1	Deposit gets blackened and spoiled.
		0.0520	0.0788 66.1		
Thymol	0.01	0.0568	0.0928 66.1	66.1	No improvement
		0.0571	0.0932 66.1		
"	0.05		Dull deposit shows a tendency to peel off
Egg-albumin	0.01 g.	0.0405	0.0664 66.0	66.0	No improvement
		0.040	0.0656 66.0		
"	0.05	—	—		Bad and dull deposit showing a tendency to peel off
Dextrine	0.005	0.040	0.0648 66.2		Slight improvement in the structure.
"	0.01	0.0401	0.0655 66.2		Bright, lustrous and fine grained deposit
"	0.05	0.0401	0.0656 66.2		Do.
"	0.10	—	—		Fine structure but brightness gets diminished.
Gelatine	0.01	0.0478	0.0814 66.0		Coarse deposit with diminished lustre
"	0.05	0.0399	0.0648 66.2		Do.
"	0.1	—	—		Do.

TABLE VIII.

Influence of methyl alcohol.

Bath = $M/2$ (after mixing). Temp. = 25° . C.D. = 15 amp./sq. ft. $p_H = 5.6$.
 Inter-electrode distance = 3.5 cm.

Amount of MeOH in 100 c.c.	Ni deposit	Cu deposit (coulometer).	Cathode efficiency.	Remarks	Sp. condy. (mhos).	Relative viscosity.	Relative density.
0.0 c.c.	0.0572 g.	0.0932 g.	66.08 %	Bright & coarse deposit.	0.0348	1.344	1.101
1.0	0.0468	0.0736	68.9	68.9 Do.	0.03411	1.370	1.098
	0.0467	0.0736	68.8				
2.0	0.0470	0.0724	70.1	70.1 Bright and fine grained deposit.	0.03271	1.398	1.096
	0.0472	0.0728	70.0				
5.0	0.043	0.0658	70.7	70.7 Do.	0.02895	1.613	1.094
	0.0431	0.0660	70.8				
10.0	0.0431	0.0664	70.5	70.5 Less shining deposit.	0.02561	1.750	1.088
	0.0431	0.0664	70.5				
20.0	0.0438	0.0676	70.09	70.1 Greyish white deposit	0.02232	1.882	1.074
	0.044	0.068	70.11				

TABLE IX.

Influence of ethyl alcohol.

Conditions same as in Table VIII.

Amount of EtOH in 100 c.c. soln.	Ni deposit.	Cu deposit (coulometer).	Cathode efficiency	Remarks.	Sp. Condy. (mhos).	Relative viscosity.	Relative density.
0.0 c.c.	0.0572 g.	0.0932 g.	66.06 %	Bright & coarse deposit	0.0348	1.344	1.101
0.5	0.0508	0.081	67.9	67.8 Do.	0.0342	1.372	1.100
	0.0532	0.085	67.8				
1.0	0.046	0.0724	69.0	68.9 Improvement in the structure.	0.0336	1.402	1.098
	0.0462	0.0728	68.8				
2.0	0.0544	0.0843	70.02	70.0 Do.	0.0323	1.451	1.096
	0.0552	0.0855	70.04				
5.0	0.0493	0.0756	70.76	70.8 Structure very fine.	0.0285	1.570	1.094
	0.0498	0.0764	70.80				
10.0	0.0497	0.0766	70.6	70.6 Do.	0.02327	1.801	1.087
	0.0498	0.0766	70.7				

TABLE X
Influence of glycerin.

Conditions same as in Table VIII.

Amount of glycerin in 100 c.c. soln.	Ni deposit.	Cu deposit (conlometer).	Cathode efficiency.	Remarks.	Sp. condy. (mhos).	Relative viscosity.	Relative density.
0.0 c.c.	0.0572 g.	0.0932 g.	66.08%	Bright & coarse deposit.	0.0348	1.344	1.101
1.0	0.0480	0.0776	67.0	67.1 Do.	0.0335	1.408	1.104
	0.0499	0.0803	67.2				
	0.0492	0.0775	68.7				
2.5	0.0432	0.0684	68.5	68.6 Do	0.0313	1.510	1.108
	0.0449	0.0706	68.9				
5.0	0.0451	0.0708	68.9	68.9 Brightness gets diminished.	0.02504	1.683	1.115
	0.0424	0.0666	68.95				
10.0	0.0425	0.0668	68.95	68.9 Grey-white deposit.	0.02255	2.076	1.130
	0.0416	0.0654	68.9				
20.0	0.0418	0.066	68.7	68.8 Do.	0.01725	2.988	1.159

TABLE XI.

Influence of mannitol.

Conditions same as in Table VIII.

Amount of mannitol in 100 c.c. soln.	Ni deposit.	Cu deposit (conlometer).	Cathode efficiency	Remarks	Sp. condy. (mhos).	Relative viscosity	Relative density.
0.0 g.	0.0572 g.	0.0932 g.	66.08%	Bright & coarse deposit.	0.0348	1.344	1.101
1.0	0.0415	0.0678	66.25	66.2 Do.	0.03389	1.377	1.105
	0.0414	0.0678	66.15				
	0.0461	0.0744	67.2				
2.5	0.0506	0.0812	67.5	67.4 Very bright and fine grained deposit.	0.03215	1.451	1.110
	0.0488	0.0782	67.6				
5.0	0.0395	0.0650	67.4	67.5 Do	0.03150	1.618	1.119
	0.0422	0.0682	67.0				
10.0	0.0423	0.0684	67.05	67.0 Do.	0.02660	1.839	1.134
	0.0390	0.070	60.3				
15.0	0.0392	0.0704	60.5	60.4 Dull, black and coarse deposit.	0.0234	2.105	1.148

TABLE XII.

Influence of sucrose.

Conditions same as in Table VIII.

Amount of sucrose deposit in 100 c.c.	Ni deposit	Cu deposit (coulometer)	Cathode efficiency.	Remarks.	Sp. condy. (mhos).	Relative viscosity.	Relative density
0.0 g.	0.0572 g.	0.0932 g.	66.08 %	Bright & coarse deposit.	0.0348	1.344	1.101
1.0	0.0434	0.0698	67.1	67.2 Do.	0.03379	1.391	1.1055
	0.0444	0.0714	67.3				
2.5	0.0426	0.0686	67.23	67.2 Fine grained deposit	0.03287	1.462	1.111
	0.0422	0.0680	67.21				
5.0	0.0372	0.0606	66.45	66.4 Do.	0.03135	1.670	1.1195
	0.0376	0.0612	66.25				
10.0	0.0420	0.0690	65.9	65.9 Coarse and granular deposit.	0.02614	1.888	1.138
	0.0286	0.0470	65.9				

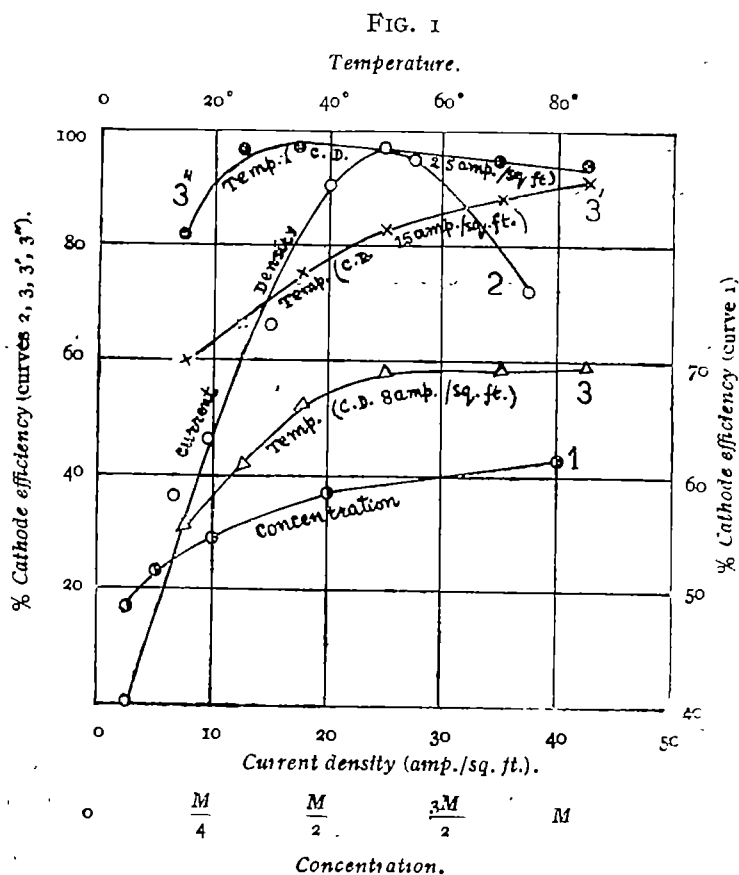
DISCUSSION.

The foregoing results show that the quality and quantity of an electrodeposit is dependent upon a large number of physical factors. These are discussed conveniently in respect of the cathode efficiency for the relevant ion, *viz.*, nickel; this is 100% under ideal conditions. Any discrepancy in this may be ascribed to the possible disturbing factors. (i) incomplete adherence of the deposit, (ii) occurrence of side reactions, *i.e.*, other than the main one for which the cathode efficiency is calculated, or (iii) solvational effects leading partly to the formation of molecular or ionic complexes in the conducting mixtures.

Electrodeposition of a metal, according to Smee, is a crystallisation process, which consists of two steps, *viz.*, (1) the formation of crystal nuclei and (2) further development of these into larger crystals. Each of these has its own velocity and the relation between these velocities determines the character of the deposit. If the velocity of (1) is greater than that of (2), a fine-grained deposit is obtained, whereas in the reverse case the deposit is coarser and the crystals big. The relation between the velocities of (1) and (2) depends, besides the factors mentioned in Table I, *i.e.*, (a) to (d), upon

(e) temperature, (f) agitation, (g) addition of foreign agents and (h) of non-electrolytes, (i) nature and structure of the base metal, (j) nature of the solvent, (k) nature of the metal deposited and (l) its valency

The results in Table IA show that bright, lustrous and adherent deposits are obtained from $M/2$ solution at the C.D. employed, stronger and dilute solutions are found to give less satisfactory results. The favourable condition for producing metallic deposits would be the presence of a large number of metallic ions. Under such conditions each crystal would be surrounded by a large number of metallic ions, so that by the passage of the current it could grow rapidly. But if fine-grained deposits are desired it is essential to select conditions which will be unfavourable to the growth of a few crystals and will thereby foster the production of a large number of smaller crystals. The condition is fulfilled, by using $M/2$ solution, when there are not at any given time many metal ions in the solution. From our



data shown in Table II (curve 1 in Fig. 1) it is seen that with the increase in concentration, $M/16$ to M , the cathode efficiency steadily increases due to increasing metal content of the bath, under the operating conditions, and corresponding diminution in hydrogen evolution at the cathode. The results in Table Ib show that with the increase in C.D. the deposit becomes finer, brighter and adherent up to a particular limit (15-40 amp./sq. ft.) after which it shows a distinct 'burning' or 'tree'-forming tendency, especially on edges and corners where the C.D. is usually much higher than the average. Loose, powdery or *burnt* deposits produced, especially when the C.D. is quite excessive, may be attributed to the formation and subsequent inclusion in the cathode deposits, of some basic material, such as the hydroxide or a basic salt of the metal, due to increased pH (or alkalinity) of the cathode film, caused by the local impoverishment of the metal or metal ion content round the cathode due to rapid depletion of the metal during the electrolysis. At very low C.D. (5 amp./sq. ft.), it is interesting to note that there was hardly any deposit of nickel, presumably due to the whole of the current being practically utilised in discharging hydrogen, which is further facilitated by too low a value of its over-voltage on iron (or nickel) as the cathode surface. It is also known that cathodic deposition of metals usually commences at their reversible potential and that at very small C.D. the discharge of positive ions may be regarded as a reversible process. At increasing C.D. the cathode potential becomes more negative partly as a result of concentration polarisation and partly on account of the slowness of one or other of the stages which must be involved between the initial discharge of the ion and the final orientation of the atom in the space lattice of the metal crystal. Volmer (*Z. physikal. Chem.*, 1928, 139, 597; 1931, 187, 165) has put forward a view that when a metal ion reaches the cathode, it is not discharged immediately but remains there on the surface between hydrated ion in the solution and that of the atom in the final state in the crystal. As a result of lateral movement over the surface the ion reaches a suitable point in the lattice where it is instantaneously discharged. From the study of the current-potential curves, obtained during the deposition of a number of metals, the conclusion has been reached that the actual neutralisation of ions occurs rapidly and that the observed polarisation is determined by the rate of formation of crystallisation nuclei by spreading across the electrode surface. If the cathode is of the same material as the metal being deposited, the points at which the ions on the surface are able to participate in the free electrons are reached without great difficulty and polarisation is not considerable. When the cathode is different from the metal being deposited, the deposition may be initially in

excess of that required when it is covered with the deposit, since there is no crystal lattice in which the ion can be discharged immediately. The anions present in the solution may possibly prevent access of the ions to the points in the lattice at which they can be discharged. This is in agreement with Barchmann's view (*Z. Elektrochem.*, 1933, **39**, 341).

The results reported in Table III (curve 2 in Fig. 1) show that at constant values for concentration and temperature, the current density exerts a pronouncedly marked influence on the cathode efficiency of nickel deposition, which varies within wide limits from zero to nearly cent per cent. Practically zero or very low efficiency at low C.D. is ascribable to the whole or appreciable part of the current being utilised in discharging hydrogen at the cathode as discussed previously. With the increase in C.D. this evolution is appreciably or even completely inhibited due to corresponding increase in hydrogen overvoltage; with further increase in C.D. the efficiency diminishes obviously due to hydrogen evolution, caused by a rapid depletion of the metal in the cathode film during electrolysis.

From the results in Table Ic it is seen that 30 minutes' time is the minimum duration of electrolysis necessary for a good and satisfactory deposition of nickel; the quantity improves in brightness and lustre up to 2 hours' duration. Too long a prolongation of electrolysis, however, leads to a decrease in the adhesiveness of the deposit, showing a tendency to 'peel' off, due to the impoverishment of the metal content round the cathode, especially in still solutions. With the decrease of inter-electrode distance the quality of the deposit improved (*cf.* Table Id).

From the study of the data shown in Tables IV A, B, C, it is seen that at any constant C.D. the quality and quantity (*cf.* curves 3, 3' and 3'' in Fig. 1) of the deposit improve by increasing the temperature up to a certain extent (about 50°) and deteriorate at higher temperatures (85°). The effect of rise in temperature in raising the efficiency at any C.D. is more marked at low than at high C.D. This can be explained by the fact that with the rise in temperature the conductivity increases due to increased mobilities of the ions with a concomitant increment in the cathode efficiency. Increase of temperature has two opposing effects; in the first place it favours the diffusion and tends to produce uniform and fine-grained deposit but on the other hand it decreases the velocity of crystal growth and thus fosters the formation of coarse deposits. At moderate temperatures the influence of the first factor is generally predominating but at higher temperature the second is increasingly operative. Slight diminution in efficiency observed at higher temperature (85°), especially at a high C.D. (25 amp /sq. ft.), might be due to hydrogen evolution caused by lowering

of its overvoltage at high temperature. The cathodic deposition of nickel, which is usually an irreversible process, especially at lower temperatures, tends to become, as the temperature rises, a reversible one. This may also account for the increased efficiency at high temperatures.

The results in Table V show that agitation caused by bubbling air under pressure through the electrolyte during the electrolysis gives quite smooth, regular, coherent and uniform deposits. The favourable effects of agitation *at a given concentration* are more marked at high than at low C.D. Similarly its effects *at a given C.D.* are more pronounced in dilute than in the concentrated solution. Similar results in nickel deposition were obtained by Ollard (*E.P.* 251010) by passing a current of ozonised air or oxygen through the electrolytic bath.

It is to be anticipated that superimposition of A.C. on D.C. during the electrolysis might reduce both the reaction resistance and the hydrogen overvoltage; its effect on the former might bring about an increase in current efficiency while its action on the latter might bring about the reverse effect. Our results (*cf.* Table V) show that A.C., when superimposed, lowers the efficiency appreciably (from 66.1 to 21% nearly). This, under the stated conditions may possibly be due to a high value for the ratio of A.C./D.C. current density, which causes a decrease in the efficiency. Similar were the conclusions of Izgarischev and Berkman (*Z. Elektrochem.*, 1925, **31**, 180) and of Kohlschutter and Schodl (*Helv. Chim. Acta*, 1922, **5**, 593). The latter workers observed no increase in the cathode efficiency of Ni deposition with lower ratio of A.C./D.C. but decrease with a higher ratio. Goodwin and Knobel (*Trans. Amer. Electrochem. Soc.*, 1920, **37**, 617) observed rapid evolution of hydrogen due to considerable diminution in its overvoltage as a result of superimposition of A.C. with sufficiently high ratio of A.C.: D.C.

A review of the literature shows that the influence of the base metal on the structure of electrodeposits, has not been fully realised. Observations by Blum and Rawdon (*Trans. Amer. Electrochem. Soc.*, 1923, **44**, 305) indicate that in general the orientation of the crystals, at least in the first layer of the deposit, is a continuation of that in the base metal. A study has, therefore, been made of the influence on the cathode efficiency and physical nature of Ni deposit of the following metals used as cathodes, *viz.*, Fe, Cu (smooth), Cu (plated), Pb, Sn, Pt (smooth), Cd (plated), Ni (plated), Co (plated), Ag, Au, Cr (plated) and Hg (plated). Our results in Table VI show that good and adherent deposits were obtained on Cu, Pb, Ni, Co, Cd, or Au-cathode; amorphous and powdery deposits were obtained on Ag and Cr cathode. The deposits on Pt cathode was unsatisfactory due to *pitting* effect. The cathode efficiency under these

conditions is in the descending order : $\text{Pb} > \text{Hg} > \text{Cu (smooth)} > \text{Cu (plated)} > \text{Cr} > \text{Co} > \text{Cd} > \text{Sn} > \text{Ni} > \text{Fe} > \text{Ag} > \text{Pt}$. It is interesting to note that there exists a rough parallelism between the cathode efficiency and hydrogen overvoltage values over the above metals. Slight but gradual diminution in the cathode efficiency as we pass on from Pb to Pt can, on the basis of hydrogen overvoltage, be attributed to gradually increasing hydrogen evolution.

No precise information is, however, available in the literature for the correlation of the cathode efficiency with the proportion of an addition agent in the electrolytic bath. This has been studied in greater details (*cf.* results in Table VII) in the case of various inorganic and organic agents, whose concentrations were varied, especially in a few cases, over a wide range. The magnitude of the above influence is illustrated by the fact that 0.025% of CrO_3 , for example, reduces the cathode efficiency from 66.1 to 0%. Various theories attempting to explain the influence of addition agents, which are generally organic or colloidal substances, exist in the literature. The possible rôle of colloidal addition agents, in general, has been discussed in a review by Blum (*Colloid Symposium Monograph*, 1921, 5, 300), who suggests the following factors for cases in which the addition agent has actually been found in the cathode deposits : "(1) Co-discharge of colloid particles and metal ions, (2) discharge of complex ions containing the metal and the colloid, (3) adsorption of colloid upon the face of the metal deposit, or (4) mechanical inclusion in the deposit." Blum further states in regard to these various possibilities that "it is difficult from the meagre data available to suggest the relative probabilities of these processes....." However, other workers have expressed preference for one or the other of the particular views outlined above. Thus Bancroft (*Trans. Amer. Electrochem. Soc.*, 1913, 23, 266) tacitly assumes that adsorption accounts for the inclusion of the addition agent in the deposit; Fuseya and Murata (*ibid.*, 1926, 50, 235) postulated the existence of complex cations formed from the metal ion and addition agent and produced evidence to show that such complex ions are doubtless formed (*cf.* also Marie and Buffat, *J. chim. phys.*, 1927, 24, 470; Taft and Mesmore, *J. Phys. Chem.*, 1931, 35, 2585). Among the causes which normally promote the production of rough and *treed* deposits is the presence of suspended impurities, especially, conducting particles of carbon, metal, etc., derived from the anodes. Upthegrove and Baker (*Trans. Amer. Electrochem. Soc.*, 1928, 53, 389) in nickel deposition have noticed that such impurities lodge themselves upon the cathode and serve as nuclei for the growth of large-grained crystals or of *trees*. Much of the effect of addition agents in reducing roughness is that of counteracting the influence of

suspended matter. The extensive studies of Mathers and his students (*ibid.*, 1912, 21, 313; 1914, 24, 117; 1915, 27, 131) upon addition agents in lead baths emphasise the fact that to a great extent the effects of addition agents are specific. With the present knowledge it is impossible to predict the exact influence of any addition agent in any particular solution.

Our results show that the addition in traces or very little amount of certain agents, *viz.*, HgCl_2 , SnCl_2 , CrO_3 , pyridine, CS_2 and acetone gives loose, powdery, black and unsatisfactory deposits. It is of interest to note that the deposit is profoundly affected by the presence in the electrolyte of even small amounts of CrO_3 . Not only is the chromic acid detrimental to the physical nature of the deposit, but also its presence to the extent of 0.02 g. in 100 c.c. reduces the cathode efficiency to 7.9% and at higher concentrations (0.025 g.) no deposit is obtained. The big fall in efficiency cannot be explained through reduction of the chromic acid, but appears, chiefly, to be related to a preferential stimulation of the discharge of the hydrogen ions. Similar were the conclusions of Macnaughtan and Hammond (*Trans. Faraday Soc.*, 1930, 26, 481). From our observations it is seen that in presence of CdCl_2 bright and lustrous deposits are obtained with increased efficiency; its increased concentration, however, produces dark deposits, which is in agreement with the earlier findings of Haring (*Trans. Amer. Electrochem. Soc.*, 1924, 46, 107) and Vozdivishenski (*J. Appl. Chem. Russ.*, 1936, 9, 1416). Addition of H_2O_2 up to 0.1% to the bath improved considerably the brightness, lustre and structure of the deposit and raised the efficiency; *pitting* effect was less noticeable. This might be due to a considerable diminution in hydrogen evolution. Its increased concentration, however, fosters the formation of dull and dark deposits by reducing the *throwing power* of the solution. The beneficial effect of H_2O_2 seems to have been noticed earlier, especially by Hans Stager (*loc. cit.*), Kohlschutter (*Helv. Chim. Acta*, 1920, 3, 614) and Potter (*loc. cit.*). Addition of $\text{Al}_2(\text{SO}_4)_3$, 18 H_2O (1%) to the bath produces marked improvement in the lustre, fineness and general character of the deposit though it causes a diminution in the cathode efficiency due to co-deposition of Al. The presence of Al in the cathode deposit was detected by the usual qualitative tests. That $\text{Al}_2(\text{SO}_4)_3$, 18 H_2O functions as the most efficient addition agent in nickel deposition may possibly be attributed to its capacity to pass into a colloidal state due to hydrolysis, as evidenced by a sudden but distinct development of opalescence in the solution and its subsequent inclusion in the cathode deposit, where its presence hinders the crystal growth, thus resulting in the formation of a fine-grained deposit. The favourable effects of this addition agent, especially in the deposition of Zn from zinc

bath have been attributed to its buffer action by Thompson (*Trans. Amer. Electrochem. Soc.*, 1926, 50, 193) who failed to detect its presence in the cathode deposit. Hard, brittle and *pitted* or *cracked* deposits obtained in the presence of very small amounts of the agents, such as, glue, thymol, egg-albumin, dextrine and gelatin (*cf.* our results) clearly indicate that a nickel depositing solution is very susceptible to the action of colloids. Phillips (*loc. cit.*) and Cuthbertson (*loc. cit.*) are of opinion that addition of organic substances are of no use to a nickel-plating bath but they make the bath complicated and hence difficult to control.

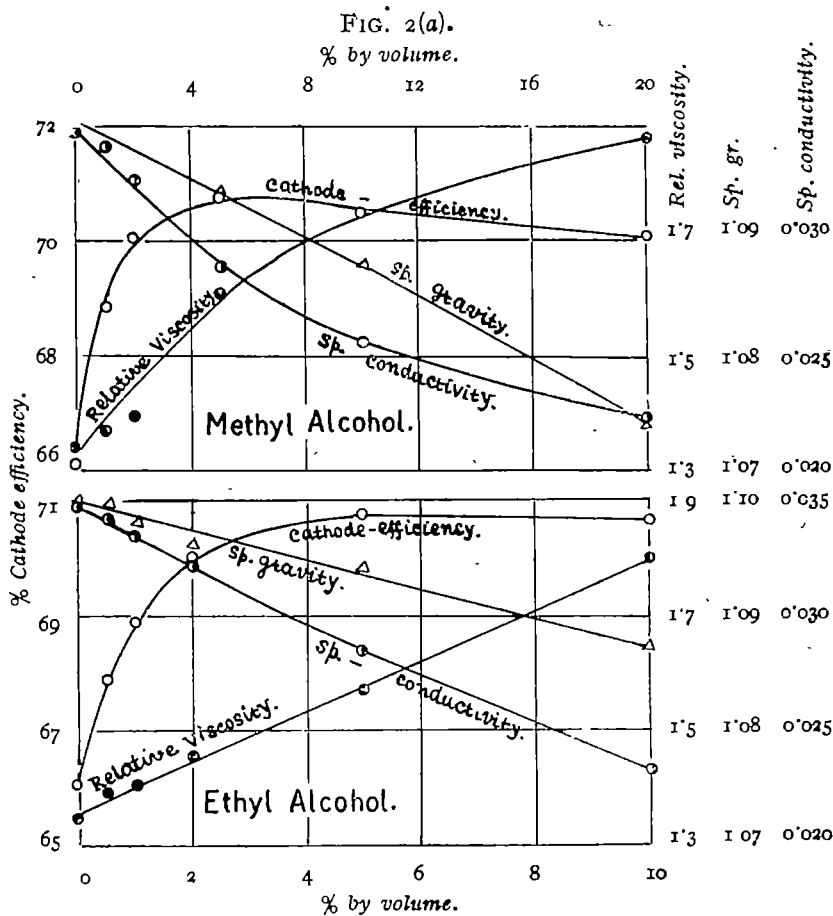


FIG. 2(b).

It is to be anticipated that the complex formation would be simpler when the addition agents were of molecular weights smaller than those characteristics of colloids. Experiments were, therefore, carried out on measurements of the cathode efficiency in the presence of varying proportion of

methyl alcohol (Table VIII and Fig. 2a), ethyl alcohol (Table IX and Fig. 2b), glycerol (Table X and Fig. 3a), mannitol (Table XI and Fig. 3b) and sucrose (Table XII). Their influence in respect of the above quantity is substantially analogous as is seen from the results. The cathode efficiency increases steadily with the progressive addition of the non-electrolyte in all cases till it approaches a limiting value; it remains practically constant being unaffected with the further addition, in the case of methyl alcohol, ethyl alcohol and glycerol but diminishes in the case of mannitol and

FIG. 3(a).

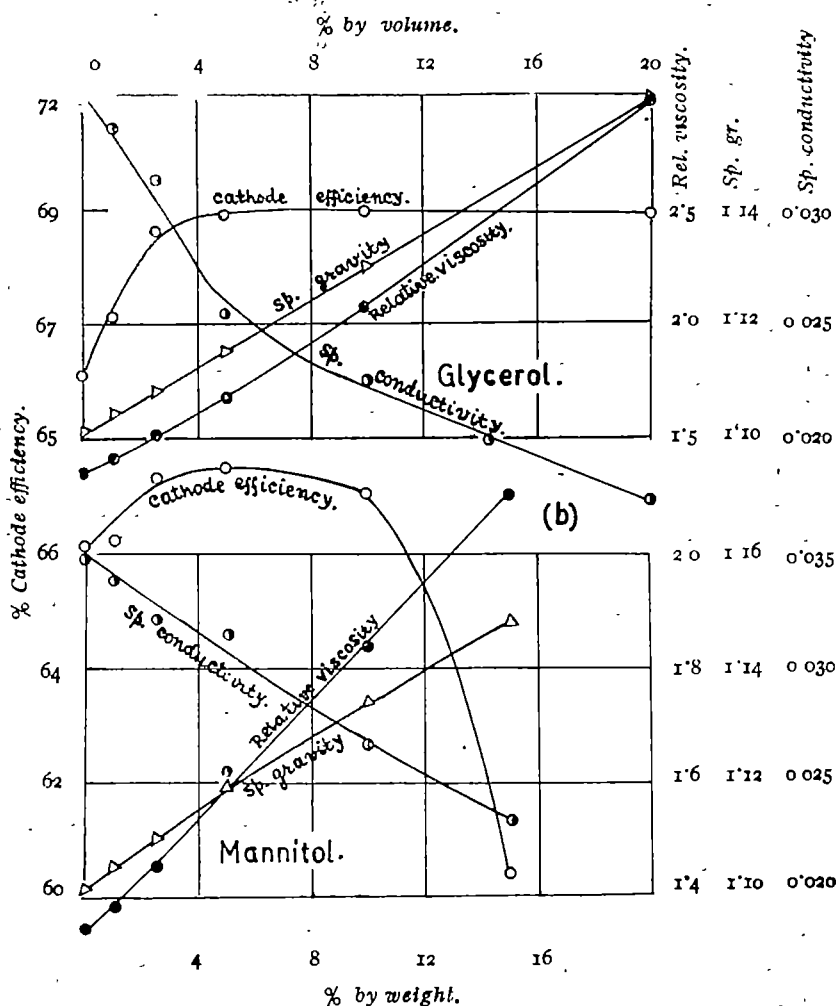


FIG. 3(b).

sucrose. The quality of the deposit also improves with the increase in concentration of the addendum up to a particular limit but deteriorates with further addition. This may be accounted for as follows. The possible disturbing factors leading to a deficit in the deposition of a metal are: (i) the existence of the cation in two forms; (ii) the dissolution of the deposited metal by the medium due to solvent action; (iii) chemical corrosion brought about by the oxygen present; or (iv) discharge of hydrogen. The loss thus brought about is a function of CaD , temperature, electrode surface, conductivity, p_H of the solution, etc., as demonstrated by the work of Hoerster and Siedel (*Z. anorg. Chem.*, 1897, **14**, 106). The addition of non-electrolyte may, however, alter the condition of the bath and bring about the diminution in the concentration of the nickel ions in the solutions thus lowering the solvent effect. It is, therefore, to be anticipated that an increase in the cathode efficiency would come about by increasing the concentration of the non-electrolyte up to a certain limiting value; our foregoing results (*cf.* curves in Figs. 2 and 3) are in agreement with this deduction. Our data with mannitol and sucrose show that the cathode efficiency after reaching the maximum values diminishes with further addition. This might be due to some interaction between the conducting material and the medium or possibly due to increased resistance of the bath solution. A number of further properties such as the conductivity, viscosity and density for the same mixtures were, therefore, studied. Schall (*Z. physikal. Chem.*, 1894, **14**, 701) found that usually the conductivity is decreased when the water of solution is replaced in part by alcohol, which is in agreement with the foregoing results. Hantzsch (*Z. anorg. Chem.*, 1900, **26**, 332) studied the influence of non-electrolytes on the conductivity of electrolytes. The addition of methyl alcohol, ethyl alcohol and acetone to aqueous solution of alkali or alkaline earth metals diminished the conductivity slightly and approximately to the same extent. Jones and Rouiller (*Amer. Chem. J.*, 1906, **36**, 427) have shown that the relative migration velocities of silver nitrate are influenced largely by the nature of the solvent, probably due to the varying degrees of combination of the solvent with one of the ions.

The specific conductivity, relative viscosity and specific gravity graphs (Figs. 2-3) show a remarkable similarity; curves showed no discontinuity. It is very likely that the occurrence of maxima in the cathode efficiency-non-electrolyte concentration curves (not revealed in other curves), might be due to the discharge of complex cation containing the metal and non-electrolyte (*cf.* previous communications from these laboratories, Joshi and co-workers, *J. Indian Chem. Soc.*, 1938, **15**, 174, 185; 1941, **18**, 177).

In conclusion the authors take this opportunity in expressing their indebtedness to Dr. S. S. Joshi, D.Sc. University Professor of Chemistry, for suggesting the problem, taking keen interest and giving valuable help and criticism during the course of this investigation.

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Received April 3, 1941.





ADSORPTIVE PROPERTIES OF SYNTHETIC RESINS. PART V.

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The adsorption of inorganic acids, bases and salts by various resins has been studied. The acids are adsorbed in the order $\text{HI} > \text{HCl} > \text{HBr}$; $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{BO}_3$, and $\text{H}_2\text{CrO}_4 > \text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$ and bases $\text{Ba}(\text{OH})_2 > \text{Sr}(\text{OH})_2 > \text{Ca}(\text{OH})_2$; $\text{KOH} > \text{NaOH} > \text{LiOH} > \text{NH}_4\text{OH}$. In the case of salts the order of adsorption of cations is $\text{Rb} > \text{K} > \text{Na} > \text{Li}$ and in anions $\text{I} > \text{Br} > \text{Cl}$. The acid-condensed phenolic resin does not adsorb the acids and salts. The order of sorption is explained on the basis of the polar concept.

Sato and Sekine (*J. Soc. Chem. Ind. Japan*, 1921, **24**, 51) and Shono (*ibid.*, 1926, **29**, 53) were the first to show the amphoteric nature of phenol-formaldehyde resins. Adam and Holms (*J. Soc. Chem. Ind.*, 1935, **54**, 1117) concluded that the positive ion was more adsorbed as hydroxide or carbonate. Bhatnagar, Kapur and Puri (*J. Indian Chem. Soc.*, 1936, **13**, 679) found that the acids were adsorbed in the order: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$ and the bases $\text{KOH} > \text{NaOH} > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3$. Akeroyed and Broughton (*J. Phys. Chem.*, 1938, **42**, 3437) had shown that in acid-condensed phenolic resin the alkalis are adsorbed in the order: $\text{NaOH} > \text{Ca}(\text{OH})_2 > \text{Ba}(\text{OH})_2$. Broughton and Lee (*ibid.*, 1939, **43**, 737) had shown that in aromatic amine-formaldehyde resin HCl is more adsorbed than H_2SO_4 .

Dubinen (*Z. physikal. Chem.*, 1929, **140A**, 81; 1930, **150A**, 145) had shown that charcoal, heated to 550° , adsorbed acids in the order: $\text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$, while heated to 800° , this order was reversed. Bartell and Fu (*J. Phys. Chem.*, 1929, **33**, 676) had shown that the polar silica adsorbed alkali in the order: $\text{LiOH} > \text{NaOH} > \text{KOH} > \text{NH}_4\text{OH}$, but it did not adsorb strong acids.

In most of the above cases no effort had been made to explain a particular order. The present work deals with the adsorption of inorganic acids, bases and salts and an attempt has been made to explain the adsorption on the concept of the polar nature of sorbate, the solvent and the resin.

EXPERIMENTAL.

The adsorption experiments were carried out with the resin prepared in the same way as in the previous paper (*loc. cit.*),

TABLE I.

Acids.	Titrated against.	Resorcinol-formaldehyde resin.			
		HCl-condensed.	NH ₃ -condensed	<i>m</i> -Phenylene diamine resin.	Protein resin.
Hydrochloric	NaOH	0.0	24.6	66.0	28.4
	AgNO ₃	0.0	25.0	66.60	29.2
Formic	NaOH	3.3	20.04	33.65	3.3
	KMnO ₄	3.15	19.80	32.80	3.2
Oxalic	NaOH	1.75	34.60	74.40	25.0
	KMnO ₄	1.60	33.85	73.50	24.6

In Table I, the estimation of acids has been carried out by two different methods, *i.e.*, either estimation of H⁺ ion by means of NaOH or of the Cl⁻ ion by AgNO₃ or of the whole molecule by KMnO₄ titrations. The agreement between the two results definitely establishes the nature of the adsorption to be molecular and not ionic in character.

The existence of undissociated molecules appears also to be supported by the refractometric investigations of Fajans. For most of the numerous electrolytes which Heydweiller (*Physikal. Z.*, 1925, 26, 529) investigated, he was not able to detect any variation of refractivity with concentration in dilute solution. The refractivity is defined as the value per mole of the Lorenz-Lorentz expression,

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{G}{d} = \frac{4\pi}{3} N \alpha_e.$$

When n is the refractive index, G , the molecular weight, d , the density, N , Loschmidt's number and α_e the polarisability of the molecule, which is the measure of the deformability of the electron shells by an electric field. Van Vleck has come to the same conclusions for gases on the basis of the new quantum mechanics. Hence the refractivity or the molar refraction is directly proportional to the polarisability of the molecule in solution.

In the previous paper (Part IV) it had already been shown that the basic resins are more polar than water, while the acid-condensed phenolic resins are less polar. In the case of basic resins at the resin-water interface, the molecule of the sorbate will orient itself in such a way that the polar group is oriented towards the resin, while the non-polar group is oriented towards water. The reverse will be the condition in acid-condensed phenolic resins. The greater the polarisability of the molecule in solution, the greater will be its adsorption. As the polarisability

increases with molar refraction, the adsorption will also increase with the molar refraction. Therefore, in basic resins, the greater the molar refraction of the sorbate in solution, the greater will be the adsorption. The reverse will hold good in the case of acid-condensed phenolic resins.

TABLE II.

% Sorption of halogens by 1 g. of resin from 100 c.c. of their 0.01 *M* aq. solution.

Halogens	Resorcinol-formaldehyde resin. HCl-condensed.	NH ₃ -condensed	<i>m</i> -Phenylene diamine resin.	Protein resin.	Molar refraction.
Chlorine	8.7	5.8	46.4	21.7	11.67
Bromine	2.0	8.0	52.0	28.0	17.43
Iodine in KI soln.	62.0	95.00	99.0	90.0	31.97

The values for molar refraction are taken from Smyth ("Dielectric Constant and Molecular Structure").

It can be seen from Table II that the adsorption of the halogens increases with the molar refraction in the case of basic resins, while it decreases in acid-condensed phenolic resin except iodine. The adsorption of iodine is abnormal practically in all the cases. Probably it may be due to its nature of forming complexes with potassium iodide.

TABLE III.

% Sorption of halogen acids by 1 g. of basic resins from 100 c.c. of their 0.01 *M*-aq. solution.

Acids.	Resorcinol-formal- dehyde resin (NH ₃ -condensed).	<i>m</i> -Phenylene diamine resin.	Protein resin.	Molar refrac- tion
HCl	25.0	66.6	29.2	6.68
HBr	14.6	48.0	20.85	9.14
HI	27.3	87.3	36.6	13.75

The halogen acids are not adsorbed by acid-condensed phenolic resin was expected.

It can be seen from Table III that the sorption of halogen acids also increases with the molar refraction except hydrobromic acid. It is well known that dissociation of HBr is too much, hence it may be expected to be least adsorbed.

It has been shown by Falkenhagen ("Electrolytes," translated by K. P. Bell, Clarendon Press, 1934 p. 319) that in aqueous solutions the free hydrated H^+ ion causes negative refractivity of +0.6 unit. The refractivity of the acids will depend on the refractivity of the anion. Therefore, in the case of acids the adsorption will also depend on the refractivity of the anion.

TABLE IV.

% Sorption of acids by 1g. of basic resin from 100 c.c. of their 0.01 *M*-aq. solutions.

Acids.	Resorcinol resin NH ₃ -condensed.	<i>m</i> -Phenylene diamine resin.	Protein resin	Refraction* for the complex ions.	Com- plex ion
HNO ₃	33.72	73.0	32.72	11.0	NO ₃
H ₂ SO ₃	24.6	65.2	24.2	5.5	$\frac{1}{2}$ SO ₃
H ₃ BO ₃	4.67	5.13	4.2	<5.5	$\frac{1}{2}$ BO ₃

* The values for the refraction of complex ions have been taken from "Dielectric Constant and Molecular Structure" by Smyth (*loc. cit.*)

It can be seen from Table IV that as the refraction of the complex ions increases, the adsorption also increases. Although no definite value for the BO₃ ion is given, it has been shown that the ionic refraction of S is 15, while that of B is 0.05. Hence it is assumed that the value for BO₃ ion would be much less than SO₃.

TABLE V.

% Sorption of acids by 1g. of resin from 100 c.c. of their 0.01 *M*-aq. solutions.

Acids.	Resorcinol resin NH ₃ -condensed.	<i>m</i> -Phenylene diamine resin	Protein resin.	Refraction for the complex ion.	Com- plex ions.
HClO ₄	33.48	81.48	35.2	13.32	ClO ₄
H ₂ SO ₄	30.0	70.0	24.8	7.31	$\frac{1}{2}$ SO ₄
H ₃ PO ₄	22.2	55.5	20.0	5.43	$\frac{1}{2}$ PO ₄
H ₂ CrO ₄	96.0	98.3	75.83	>13.32	$\frac{1}{2}$ CrO ₄

In Table V also the adsorption increases with the refraction of the complex ions. The refraction of the chromate ion was not determined because of its uncertainty due to proximity to an absorption band. Hence no definite value is given to it. The order of sorption of acids is $HCl > HClO_4 > H_2SO_4 > H_3PO_4 > HNO_3 > H_2SO_3 > H_3BO_3$ and $H_2CrO_4 > HClO_4 > H_2SO_4 > H_3PO_4$.

TABLE VI.

% Sorption of alkali halides by 1g. of resin from 100 c.c. of their 0.01 *M*-aq. solution.

Cation.	Resorcinol-formaldehyde resin (NH ₃ -condensed)			<i>m</i> -Phenylenediamine resin			Protein resin.		
	Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
Li	0.0	1.00	2.50	0.92	3.14	5.48	0.46	1.85	3.8
Na	0.47	1.90	2.80	1.88	4.25	5.74	0.94	2.5	4.2
K	0.93	2.10	3.0	2.77	5.10	6.25	1.25	2.7	4.6
Rb	1.85	2.30	3.2	3.7	5.30	6.70	2.00	3.0	5.0

TABLE VII.

Molar refractions (NaD line) of alkali halides at infinite dilution.

Cation.	Cl.	Br.	I.
Li	8.58	12.25	18.82
Na	9.2	12.87	19.44
K	11.23	14.90	21.47
Rb	12.58	16.25	22.82

* The values are taken from "Dielectric Constant and Molecular Structure", by Smyth, p. 145.

It can be seen from Tables VI and VII that the adsorption increases with the molar refraction. The order of sorption of cations is Rb>K>Na>Li and of anion is I>Br>Cl.

The acid-condensed phenolic resin did not adsorb the acids and the salts.

TABLE VIII.

% Sorption of alkalis by 1g. of resin from 100 c.c. of their 0.01 *M*-aqueous solutions.

Alkalis.	Resorcinol-formaldehyde resin		Refractive index.	Molar refraction.
	HCl-condensed.	NH ₃ -condensed.		
LiOH	91.45	83.67	1.3375	3.11
NaOH	92.53	86.34	1.3380	3.915
KOH	94.32	88.27	1.3427	5.803
NH ₄ OH	70.36	52.86	1.3326	

It can be seen from Table VIII that the adsorption of alkalis also increases with the molar refraction. The adsorption of ammonia is the least. Although its molar refraction is not yet known it can be seen from the refractive indices that its adsorption should be the least.

TABLE IX.

% Sorption of alkalis by 1g. of resin from 100 c.c. of their 0.01 *M*-aq. solutions.

Alkalis.	Resorcinol formaldehyde resin		Protein resin	Molar refraction.
	HCl-condensed.	NH ₃ -condensed.		
Ca(OH) ₂	98.45	90.81	56.12	8.425
Sr(OH) ₂	99.00	91.66	57.02	39.44
Ba(OH) ₂	99.57	93.68	59.69	43.68

Table IX shows the adsorption of Ca (OH)₂, Ba(OH)₂, Sr(OH)₂. Here too the adsorption increases with the molar refraction.

So it can be seen from all the above results that the adsorption increases with the molar refraction. The results fully corroborate the polar concept discussed in our previous paper.

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Received June 6, 1941.

SOME NEW REACTIONS OF 1-BENZYLIDENECOUMARAN-2-ONES. PART I.

By T. B. PANSE, R. C. SHAH AND T. S. WHEELER.

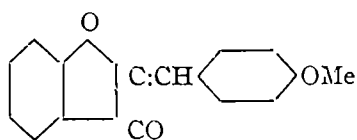
Examination of the reactions of 1-*p*-anisylidene-coumaran-2-one indicates that the reactions characteristic of the keto-ethylene group exhibited by chalcones are unaffected by the cyclic linkage. Thus one of the bromine atoms in its dibromide, like the halogen atom in the chalcone dibromides, is readily replaced by alkoxyl on treatment with methyl or ethyl alcohol. It also undergoes, like chalcones, Michael additions with cyclohexanone and desoxybenzoin and condenses with ethyl acetoacetate.

Chalcones contain an unsaturated keto-ethylene group. The reactivity of this group in chalcones has been studied extensively. Benzylidene coumaran-2-ones also contain a partially cyclised keto-ethylene group. It seemed worthwhile studying with benzylidene-coumaran-2-ones, a number of typical reactions of chalcones in order to find out whether the characteristic reactions of the keto-ethylene group exhibited by chalcones are affected by the partially cyclised keto-ethylene group. The results of the study of a typical 1-*p*-anisylidene-coumaran-2-one (I) show that benzylidene-coumaran-2-ones behave like chalcones and the cyclic linkage of the keto-ethylene group does not affect the reactions of the keto-ethylene group.

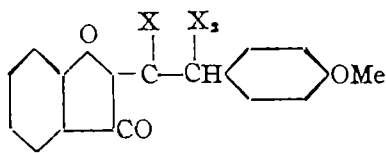
Thus (I), which contains a *p*-methoxy group in the benzylidene nucleus, on bromination forms a dibromide (II), the bromine atom in which, like the halogen atom in phenyl-*p*-(or-*o*)-alkoxystyryl ketone dibromides (alkoxychalcone dibromides), is readily replaced by alkoxyl on treatment with alcohols (see Warrair *et al.*, *J. Chem. Soc.*, 1937, 1798) and the resulting product has been assigned the constitution (II, $X_1 = \text{Br}$; $X_2 = \text{O} - \text{Alkyl}$) *viz* α -bromo- β -alkoxy derivative.

(I) like chalcones also undergoes normal Michael addition with cyclohexanone and desoxybenzoin (*cf.* Hill, *J. Chem. Soc.*, 1935, 1115) to yield (III, $R_1 = \text{CO} \cdot (\text{CH}_2)_4 \cdot \text{CH}_2$) and (III, $R_1 = \text{Ph} \cdot \text{CO} \cdot \text{CH} \cdot \text{Ph}$) respectively.

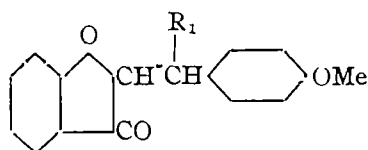
(I) like chalcones also condenses with ethyl acetoacetate to give a cyclohexenone derivative (IV) (*cf.* Knoevenagel, *Annalen*, 1894, 281, 58). The structure assigned to (IV) is based on the chalcone analogy (*cf.* Rao and Wheeler, *J. Chem. Soc.*, 1939, 1004) and is supported by its reactions with dinitrophenylhydrazine and similar other ketonic reagents.



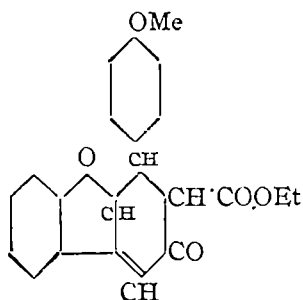
(I)



(II)



(III)



(IV)

E X P E R I M E N T A L

1-*p*-Anisylidene-coumaran-2-one (I) was prepared as described by Herstein and Kostanecki (*Ber.*, 1899, **32**, 318).

Bromination of 1-p-Anisylidene-coumaran-2-one.—(I), when treated in cold chloroform solution with the theoretical quantity of bromine in the same solvent, yielded 1-bromo-1-(ω -bromo-*p*-methoxybenzyl)-coumaran-2-one (II, $X_1=X_2=Br$), m.p. (chloroform), 148° . (Found: Br, 39.1. $C_{18}H_{12}O_3Br_2$ requires Br, 39.0 per cent).

*Action of Alcohols on 1-Bromo-1-(ω -bromo-*p*-methoxybenzyl)-coumaran-2-one.*—The dibromide when boiled with methyl or ethyl alcohol for $\frac{1}{2}$ hour gave respectively on cooling 1-bromo-1-(ω -*p*-dimethoxybenzyl)-coumaran-2-one, m.p. (methyl alcohol), 137° (Found: Br, 22.2. $C_{17}H_{16}O_4Br$ requires Br, 22.0 per cent) and 1-bromo-1-(*p*-methoxy- ω -ethoxybenzyl)-coumaran-2-one, m.p. (alcohol), 145° . (Found: Br, 21.4. $C_{18}H_{17}O_4Br$ requires Br, 21.2 per cent).

*Action of Alkali on 1-Bromo-1-(ω -bromo-*p*-methoxybenzyl)-coumaran-2-one: Formation of 4'-Methoxyflavonol*—To a hot alcoholic solution of the dibromide (1 g.) was added *N*/10- potassium hydroxide (125 c.c.). The cold liquid on acidification gave the 4'-methoxyflavonol. It was crystallised from alcohol, m.p. 223° (*cf.* Auwers and Pohl, *Annalen*,

1914, 405, 243). Edelstein and Kostanecki (*Ber.*, 1905, 38, 1509), who prepared it in a different way, record its m.p. as 225°.

Condensation of 1-p-Anisylidene-coumaran-2-one with cycloHexanone.—To a boiling alcoholic solution of (I) (5 g.) and cyclohexanone (10 c.c.) was added an aqueous sodium hydroxide solution (50 %, 10 g.). On allowing to cool the reaction mixture overnight, 1-[*p*-methoxy- ω -(2'-keto-1'-cyclohexyl)-benzyl]-coumaran-2-one separated. It was filtered, washed with water and crystallised from alcohol, m.p. 278°. (Found : C, 75.7 ; H, 5.8. $C_{22}H_{22}O_4$ requires C, 75.4 ; H, 6.3 per cent).

Condensation of 1-p-Anisylidene-coumaran-2-one with Desoxybenzoin.—The alcoholic solutions of (I) (5 g.) and desoxybenzoin (5 g.) were mixed and heated at the boiling point for $\frac{1}{2}$ hour. While still hot, sodium ethoxide (1.25 g. sodium) was added to it. The reaction mixture, on cooling, yielded 1-(β -benzoyl- β -phenyl- α -*p*-anisyl- α -ethyl)-coumaran-2-one (III, $R_1 = Ph \cdot CO \cdot CH \cdot Ph$) in crystalline form. It was recrystallised from acetone, m. p. 243°. (Found : C, 77.5 ; H, 5.4. $C_{30}H_{24}O_4$, H_2O requires C, 77.3 ; H, 5.5 per cent).

Condensation of 1-p-Anisylidene-coumaran-2-one with Ethyl Acetoacetate.—An alcoholic solution of (I) (5 g.), ethyl acetoacetate (6.3 c.c.) and sodium ethoxide (0.62 g. sodium) was heated under reflux for 4 hours and kept overnight. Next day, crystals of ethyl 2-*p*-anisyl-3 : 4-(1' : 2'-coumarano)- Δ^4 -cyclohexen-6-one-1-carboxylate (IV) separated from the solution. On recrystallisation from alcohol, it melted at 159°. (Found : C, 72.4 ; H, 5.6. $C_{22}H_{20}O_5$ requires C, 72.5, H, 5.5 per cent). It gives cherry-red colouration with alcoholic ferric chloride.

Hydrolysis and Decarboxylation of (IV).—The condensation product (IV) (0.5 g.) was heated with 10 % hydrochloric acid (20 c.c.) in a sealed tube under pressure at 160° for 5 hours. On cooling, the contents of the tube were obtained as a sticky mass which was filtered, washed with water and sodium bicarbonate solution. The 5-*p*-anisyl-3 : 4 (2' : 1'-coumarano)-cyclohexen-1-one, so obtained, was crystallised from alcohol in needles, m.p. 152°. (Found : C, 78.1 ; H, 5.9 ; $C_{19}H_{16}O_3$ requires C, 78.0, H, 5.5 per cent).

The compound (IV) also yielded the following derivatives :

Semicarbazone, m.p. (after being washed with hot alcohol) 253° 55°. (Found : N, 9.9 ; $C_{23}H_{23}O_5N_3$ requires N, 10.0 per cent).

Oxime, m.p. (80 % alcohol), 183° (decomp.). (Found : N, 3.7. $C_{22}H_{21}O_5N$ requires N, 3.7 per cent).

2:4 *Dinitrophenylhydrazone* (yellow crystals), m.p. (acetic acid), $209^{\circ}-10^{\circ}$ (decomp.). (Found: N, 10.2. $C_{28}H_{24}O_8N_4$ requires N, 10.2 per cent). The *copper salt* of (IV) which was obtained by shaking (IV) in ethereal solution with an equal weight of copper acetate in aqueous solution for 6 hours had, after being washed with hot water, a melting point of 210° . It is soluble in benzene. [Found: Cu, 7.6. $(C_{22}H_{16}O_8)_2Cu$ requires Cu, 7.9 per cent.]

One of us (T.B.P.) thanks the University of Bombay for the award of a research grant.

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Received June 6, 1941.

RAMAN SPECTRA OF SUBSTITUTED SULPHURIC ACIDS. PART I.

BY JAGANNATH GUPTA AND ANIL KUMAR MAJUMDAR.

The Raman spectra of $\text{NH}_2\text{SO}_3\text{H}$ and $\text{NH}_2\text{SO}_3\text{Na}$ have been photographed under different conditions. It is found that the tetrahedral structure of the sulphates persists in the amino derivative. Force constants have been calculated and their significance discussed.

Interesting differences in the Raman spectra of sulphates and bisulphates were observed by previous workers (Nisi, *Jap. J. Phys.*, 1929, 8, 119; Woodward, *Physikal. Z.*, 1931, 32, 777) which might be due to differences of small magnitude in the ionic structures. The present investigation has been taken up with the purpose of studying the effect of partial and gradual substitution in the sulphato group on its structural characteristics. Houlton and Tartar's work on the Raman spectra of ethyl and higher alkyl sulphonates and sulphinates (*J. Amer. Chem. Soc.*, 1938, 60, 544) show the effect of alkyl substitution, although data on the methyl derivative are lacking. The effect of substitution by amino groups is the object of study of the present work.

The simplest amino derivative of sulphuric acid is aminosulphonic acid ($\text{NH}_2\text{SO}_3\text{H}$), which forms stable, colourless, anhydrous crystals at room temperatures, and is now well known as a very suitable primary acidimetric standard. Conductometric and pH measurements (Sakurai, *J. Chem. Soc.*, 1896, 69, 1654; Cupery, *Ind. Eng. Chem.*, 1938, 30, 627) indicate that it is quite a strong acid, comparable to sulphuric acid itself.

At ordinary temperatures, an aqueous solution of the acid is quite stable, appreciable hydrolysis being detectable after a week. Alkaline solutions, however, slowly hydrolyse to sulphates. In all cases decomposition is favoured by a rise of temperature.

The Raman spectra of the acid and its sodium salt have been examined under different conditions, the results of which are reported in the present paper.

EXPERIMENTAL.

The acid was easily prepared by the action of fuming sulphuric acid on urea (Baumgarten, *Ber.*, 1936, 69, 1929). The precipitated crystals were purified by recrystallisation from water (m.p. 205°). A large single crystal (measuring $12 \times 9 \times 3$ mm.) was prepared by slow evaporation of

the aqueous solution and kindly lent to us by Dr. P. B. Sarkar. The faces of this crystal were polished by carefully rubbing it on a piece of moist cloth, and were protected by coating with a thin layer of white vaseline. An exposure of 24 hours with the unfiltered radiation from a quartz-mercury arc lamp yielded a fairly intense spectrum.

Solvents used for examining the solutions were all freshly distilled before work. The aqueous solutions (50%) were repeatedly filtered directly into the Wood's tube to obtain it free from suspended impurities. The methyl alcoholic solution (25%) of the acid was filtered through a glass-sintered gooch crucible instead of through a filter paper. Each solution was qualitatively tested before and after exposure, which varied from 24 to 40 hours, and found free from sulphate. In examining the solutions, the radiations from the mercury arc were filtered through a 4% solution of *m*-dinitrobenzene in benzene to cut off the 4047 Å group of lines. In spite of all attempts, the spectrum of the alcoholic solution was unsatisfactory, due to a strong continuous background masking the Raman lines. The results are given in the following table.

TABLE I.

(Raman lines in cm^{-1})

P=polarised. $\rho \ll 0.5$; D=completely depolarised.

Crystal.	Aq. soln.	ρ .	Soln. in MeOH (incomplete)	Sodium sulphamate 'aq. soln.'
352 (2b)	380 (2)	D		393 (1)
535 (2)				
550 (2)	545 (3)	D		570 (1)
677 (1)				
604 (1)	714 (1)	D		
1054 (58)	1072 (6)	P	1068 (1)	969 (1)
1271 (1)	1310 (1)	D		1037 (2)
3080-3180 (2b)				

Figures in parenthesis indicate approximate relative intensities estimated visually. With a standard polarisation set-up, using a Wollaston prism, the spectrum of the acid solution was photographed to ascertain the polarisation characteristics of the lines qualitatively, and the results are shown in column 3, Table I.

DISCUSSION.

It may be observed that the spectra of the acid and its salt are similar but not identical, and do not agree on many points with those recorded previously by Angus, Leckie and Williams (*Trans. Faraday Soc.*, 1938, **34**, 793). The line at 1357 cm^{-1} in the spectrum of the acid is very weak and completely vanishes in that of the salt, and is therefore attributed to a deformation vibration of the hydroxy group. Among the other lines recorded, it may be remarked that the difference between the spectra of the acid and its salt is less than that between sulphuric acid and sulphates of the same concentrations (*cf.* Hibben, *Chem. Rev.*, 1933, **13**, 404), but is greater than that between the bisulphates and sulphates (Fadda, *Nuovo cimento*, 1932, **9**, 168). Polarisation photograph shows that in the solution of the acid, the intense line at 1065 cm^{-1} is highly polarised, while the rest are completely depolarised. These observations indicate that the structure of the sulphamic acid molecule is essentially tetrahedral, and is not greatly changed in the formation of the ionised salt, although minor distortions in structure are quite probable. The large shift of one of the three-fold degenerates (ν_3) from 714 in the acid to 969 in the salt is remarkable, the spectrum of the latter being a closer approach to that of the sulphate.

The force constants of the tetrahedral molecules of the acid and its salt have accordingly been calculated using the central force system (*cf.* Kohlrausch, *S.R.E.*, 1931, p. 213), the reasonable assumption being made that the valence forces of the central sulphur atom are identical. The results obtained lend support to this assumption of complete identity of the purely co-valent link $\text{S}-\text{NH}_2$ and the co-ordination links with the oxygen atoms, since the spectrum resembles that of a regular tetrahedron rather than of a symmetrical top. In Table II have been tabulated these constants along with that obtained from the data of allied substances.

TABLE II.

	$f \times 10^{-5}$.	$f \times 10^{-5}$.
SO_4^{2-}	4'6	1'14
HSO_4^-	4'5	1'47
NH_2SO_3^-	4'93	1'31
$\text{NH}_2\text{SO}_3\text{H}$	4'07	1'67

If on the strength of the results obtained with the sulphate and the bisulphate ions, it is assumed that a distortion of the regular tetrahedron is marked by a falling off of the central force and a corresponding increase in the deformation constant, it follows that the aminosulphonate ion is a more regular tetrahedron than the free acid. It is, however, usually found that in perfectly regular tetrahedral molecules, $\nu_3 > \nu_1$ while the opposite is being observed here. A permanent departure from a regular tetrahedral structure may not therefore be improbable in aminosulphonic acid and to a lesser degree in its anion. It may also be observed that in the spectrum of the crystal of the acid, some of the degenerates are split up due probably to the anisotropic field of the distorted tetrahedra.

The case for the formation of a protropic isomer of aminosulphonic acid of the type $\text{'NH}_3\text{'SO}_3^-$ is not clear from the optical data available up till now, although the possibility is by no means excluded. Infra-red absorption at 3.15μ is often identified with the NH_2 group, but is seen to persist in glycine where the group presumably becomes NH_3^+ ; the sulphamic acid crystal shows absorption at 3.17μ (Buswell, Downing and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2759), on which observation therefore any deduction regarding proton shifting is uncertain. In the Raman spectrum of the anhydrous crystal examined by us, a broad band at $3080\text{--}3180\text{ cm}^{-1}$ has been observed, which must be due to hydrogen oscillations against nitrogen or oxygen. The O—H frequencies are known to be in close proximity to the N—H and to suffer large deviations in value depending on the state and structure of the molecule; *e.g.*, water shows a very broad band at 3400 cm^{-1} which shifts to 3100 cm^{-1} in ice (Sutherland, *Proc. Roy. Soc.*, 1933, **141A**, 535). The broad band at $3080\text{--}3180\text{ \AA}$ observed in the acid crystal may, on the other hand, indicate the formation of an NH_3^+ ion as was pointed out by Edsall (*J. Chem. Phys.*, 1937, **5**, 225) in his study of the organic amine hydrochlorides.

The authors are indebted to Prof. M. N. Saha, Palit Professor of Physics, for all laboratory facilities and to Dr. P. B. Sarkar and Dr. S. C. Sirkar for their kind interest in the work.

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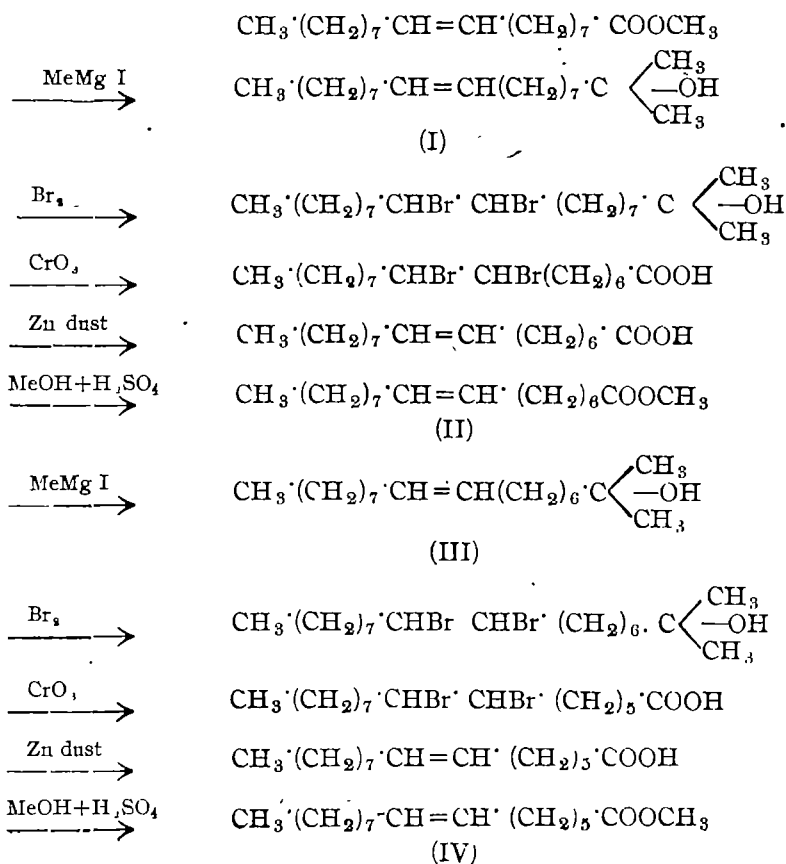
Received May 20, 1941.

STUDIES IN LONG-CHAIN ACIDS. PART III. ON *BIS-NOR-OLEIC* ACID

BY P. C. MITTER AND PHANINDRA NATH BAGCHI.

Δ^6 -Hexadecenoic acid (*bis-nor-oleic* acid) has been synthesised from oleic acid by subjecting it to a two stage Wieland degradation.

As a starting material for some synthetic operations, we were in need of $\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CH} = \text{CH} \cdot (\text{CH}_2)_5 \cdot \text{COOH}$, Δ^6 -hexadecenoic acid (*bis-nor-oleic* acid). Such an acid is not known to occur in nature. Direct synthesis of an acid of this composition being difficult, we thought of subjecting oleic acid to a two-stage Wieland degradation, as follows, when the acid in question was obtained.



The method of preparation was, however, found unsuitable for our purpose as the starting material namely oleic acid was difficult to obtain in a sufficiently pure form and the isolation and the purification of both *nor*-oleic and *bis-nor*-oleic acid was difficult. Besides, the yields in the two intermediate oxidation operations were unsatisfactory (*vide* experimental.)

EXPERIMENTAL.

I: 1-Dimethyl- Δ^9 -octadecenol-1(I).—A Grignard solution (4 mol.) was prepared from magnesium (32 g.) in ether (500 c.c.) and methyl iodide (100 c.c.) in ether (150 c.c.) and a solution of methyl oleate (100 g.) in ether (150 c.c.) was added to this drop by drop under ice-cooling. The reaction was not very vigorous and no precipitate of the Grignard complex separated. The mixture was kept overnight and then heated under reflux on the water-bath for 2 hours when a small quantity of a precipitate was obtained. After cooling, the reaction mixture was poured into a cooled solution of ammonium chloride and then treated with hydrochloric acid. The ethereal layer was separated, washed with water and bicarbonate solution, the ether evaporated and the residue hydrolysed with 5% methyl alcoholic caustic potash. The oily product, obtained after the addition of water, was thrice extracted with ether. The ethereal solution was dried (sodium sulphate) and evaporated. On distilling the residue, the main fraction distilled over between 167° and 175° at 3-4 mm. with a very small forerun of a more mobile liquid with a characteristic odour, which is probably the corresponding unsaturated hydrocarbon. On redistillation, the carbinol was obtained as a colourless limpid oil with a very faint odour, b.p. 167° - $172^\circ/3$ mm., yield 80 g. [Found: C, 79.8, 79.7; H, 13.4, 13.4; Iodine value (Wijs), 89, 87. $C_{20}H_{40}O$ requires C, 81.1; H, 13.5 per cent. Iodine value, 86].

The analytical data in this as well as in the subsequent preparations were not very satisfactory due to the fact that the oleic acid, which was the starting material, always contains other fatty acids which are very difficult to separate by fractional distillation. Nevertheless, the almost theoretical iodine value indicated that the substance was not very impure.

Methyl Δ^7 -Heptadecenoate (Methyl *nor*-oleate) (II).—The carbinol (30 g.) was dissolved in acetic acid (250 c.c.) and a solution of bromine (5.7 c.c.) in glacial acetic acid (110 c.c.) was added drop by drop, under cooling. There was immediate decolourisation at the beginning but after the addition

of bromine was complete, a faint colour persisted. The solution was next heated on the water-bath and chromic acid mixture, prepared by dissolving 58 g. of chromic anhydride (80-85%) in 35 c.c. of warm water and diluting with 375 c.c. of acetic acid, was added in course of 2½ hours with occasional shaking. When the addition was complete the mixture was heated for further 3 hours; some rectified spirit was added to remove excess of CrO_3 and the acetic acid removed as far as possible under reduced pressure. The residue was warmed with dilute sulphuric acid and then extracted with ether. The ethereal solution was washed with water (if a slight emulsion was formed it was broken up by the addition of salt), the ether removed and the residue dried in a vacuum desiccator and weighed. It was then dissolved in 225 c.c. of glacial acetic acid, zinc dust (35 g.) added and the solution heated on the water-bath for 2 hours after which it was filtered hot. Acetic acid was then removed in *vacuo*, the residue treated with dilute sulphuric acid to decompose any zinc salt formed and the mixture extracted with ether. The ethereal extract was washed twice with water and then thrice with *N*-NaOH solution. The alkaline solution was concentrated and treated with salt when sodium nor-oleate salted out. This was filtered, decomposed with dilute sulphuric acid, extracted with ether and the ethereal solution washed with water, dried (sodium sulphate) and evaporated. The product (10 g.), after drying in a vacuum desiccator, was esterified with methyl alcohol (50 c.c.) and concentrated sulphuric acid (*d* 1.84, 5 c.c.) by heating under reflux for 4 hours. The product was worked up as usual and then distilled and the fraction boiling between 158° — $167^\circ/6$ mm. collected. On redistillation, it boiled between 159° — 165° at 6 mm., yield 5 g. The ester readily decolourises bromine and permanganate. (Found: C, 75.5, 75.7; H, 11.5, 11.7. $\text{C}_{16}\text{H}_{34}\text{O}_2$ requires C, 76.6; H, 12.0 per cent).

1: 1-Dimethyl- Δ^8 -Heptadecenol-1(III).—This was prepared from methyl nor-oleate (10 g.) and methyl magnesium iodide (from 4 g. of magnesium and 13 c.c. of methyl iodide) in a manner exactly similar to that described under the other carbinol. After the removal of the unreacted methyl nor-oleate the residue was distilled and the portion boiling between 158° — 164° at 4 mm. collected separately. On redistillation, it boiled at 160° — $164^\circ/4$ mm., yield 8 g. (Found: C, 79.8; H, 13.2. Iodine value, 91. $\text{C}_{16}\text{H}_{32}\text{O}$ requires C, 80.8; H, 13.5 per cent. Iodine value, 90).

Methyl Δ^8 -Hexadecenoate (IV).—1: 1-Dimethyl- Δ^8 -heptadecenol-1 (9.5 g) in glacial acetic acid (30 c.c.) was brominated with bromine (1.8 c.c.) in glacial acetic acid (60 c.c.) and then treated with a mixture formed by dissolving chromic acid (21 g.) in warm water (18 c.c.) and then diluting

with acetic acid (130 c.c.). The oxidation mixture was worked up as before and then debrominated with zinc (9 g.) in acetic acid (80 c.c.). The debrominated acid was extracted from the ethereal solution with sodium hydroxide solution and then salted out. The sodium soap was decomposed in the usual way and the acid, after separation, was esterified with methyl alcohol and sulphuric acid. After two distillations, the ester boiled at 150° - 155° /6 mm. The ester decolourises bromine and permanganate solution. (Found: C, 75.3; H, 11.5. Iodine value, 96. Calc. for $C_{17}H_{32}O_2$: C, 76.1; H, 11.9 per cent. Iodine value, 95)

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Received October 5, 1939.

THE EFFECT OF COLLOIDS ON THE ELECTRO-DEPOSITION OF NICKEL ON COPPER.

BY V. S. PURI AND S. R. SETH.

The effect of chromium, molybdenum, tellurium and tungsten sols on the electro-deposition of nickel has been investigated and the nature of the deposits studied.

The action of inorganic colloids on the electrodeposition of nickel on copper has been investigated in this laboratory by Puri and co-workers (*J. Indian Chem. Soc.*, 1939, **16**, 71, 581; 1940, **17**, 699; Sir S. S. Bhatnagar Commemoration Vol., 1941, p. 33, 59) and the results have been very satisfactory. The basic idea of this study is to find a colloid, the addition of which to the nickel plating bath, should make the deposit hard, smooth and shining and also make the electroplating of nickel easier and cheaper.

The effect of sulphur, selenium and iodine sols has been studied previously. In the present investigation the effect of chromium, molybdenum, tellurium and tungsten sols has been studied.

EXPERIMENTAL.

The bath employed and other experimental details were the same as used by us previously (Puri and Seth, *loc. cit.*). A current of 0.2 ampere was used throughout the experiment.

Preparation and Concentration of the Colloids.

Chromium Hydroxide Sol.—Ammonia was added to a boiling solution of chromium chloride to precipitate $\text{Cr}(\text{OH})_3$. Excess of ammonia was expelled. The precipitate was filtered and thoroughly washed. Half of the precipitate was dissolved in hydrochloric acid and the rest added to it. CrCl_3 peptised the precipitate. On dilution a beautiful green sol was obtained. This was positively charged. (Neidle and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 1962; 1917, **39**, 71). The sol was estimated as Cr_2O_3 .

Molybdenum Sol.—It was obtained by the peptising action of dilute hydrochloric acid on the metal formed by the reduction of the oxide with zinc dust. The dialysed sol was light brown in transmitted light and grey in reflected light. The sol was found to be positively charged (Wedekind and Jochem, *Z. angew. Chem.*, 1927, **40**, 434).

Tellurium Sol.—Telluric acid (0.5 g.) was suspended in 50 c.c. of boiling water to which was added hydrazine hydrate drop by drop until turbidity

occured. It was diluted to 250 c.c. when a rich brown sol was obtained. This was negatively charged (Doloan, *J. Phys. Chem.*, 1925, **29**, 178).

Tungsten Trioxide Sol.—Sodium tungstate was acidified in cold with dilute hydrochloric acid when a yellow gel was thrown down. Repeated washings peptised the gel. It was negatively charged (Van Bemmelen's *Gedenkbuch*, 1910, p. 152; *Kolloid Z.*, 1914, **18**, 145).

Manganese Dioxide Sol.—It was obtained by adding slowly 100 c.c. of 6% potassium permanganate to a cold solution containing 5 g. of glucose in 20 c.c. of water together with a few c.c. of 10% sodium hydroxide. The mixture became rapidly viscous and after some time changed to a stable limpid sol (Witzemann, *J. Amer. Chem. Soc.*, 1915, **37**, 1079; 1917, **39**, 27).

Effect of Colloids.

Chromium Hydroxide Sol—With 3 c.c. the deposit is hard and shining but there are a few black specks here and there. With 5 c.c. there is a definite reduction in grain-size. The deposit is close-grained and microcrystalline. Even the side, opposite to the cathode, shows good deposit. Addition of 7 c.c. of the colloid diminished the brightness indicating that the maximum quantity of the colloid has been added.

Molybdenum Sol.—With 5 c.c. the deposit is very bright and hard. The surface is smooth and lustrous. Addition of 7 c.c. of the colloid decreases the lustre, while with 10 c.c. the brightness vanishes and the deposit looks pretty dull.

Tellurium Sol.—Its results are comparable to selenium sol. With 5 c.c. the deposit is very shining, coherent and microcrystalline. All the defects in the original plate disappeared. The surface could take a high polish. Addition of 10 c.c. of the colloid gives a coherent and shining deposit, but its brightness slightly decreases. On the addition of 15 c.c. the crystal size increases and the deposit becomes coarse and less hard, indicating that optimum concentration of the colloid has reached.

Tungsten Trioxide Sol.—The addition of 1 c.c. of this sol makes the nickel deposit shining and hard. With 3 c.c. of the colloid the deposit is quite good but not very thick as at places the surface of copper is visible. With 5 c.c. of the colloid effect is more potent, the deposit is very bright and adherent and microphotographs show a considerable reduction in grain-size. The addition, however, of 7 c.c. of the colloid makes the deposit non-coherent and crystalline (*vide* table below).

Manganese Dioxide Sol.—Addition of 5 c.c. of the colloid improves the hardness of the deposit but does not effect the brightness at all; addition of

7 c.c. improves the lusture and gives an ideal deposit with this colloid. Addition of 10 c.c. again diminishes the lusture.

The table below indicates briefly the quantity of colloid used in each case and the effect on the nature of the deposit.

Colloid	Colloid added.		Ni deposited.		Nature of the deposit
	(c.c.)	(g./400 c.c.)	Actual.	Calc.	
Nil	0	0 00	0'1132 g	0'1141 g.	Deposit is shining Abrasion marks visible.
Chromium hydroxide sol	3	0'000048	0'1131	0'1161	Deposit very hard and shining.
	5	0'000080	0'1061	0'1084	Ideal deposit. Very shining and hard, micro crystalline. Defects of original plate absent.
	7	0'000112	0'1124	0'1163	Deposit less shining and crystalline.
	10	0'000144	0'1061	0'1084	Deposit less shining and crystalline.
Molybdenum sol	5	0 0025	0'0974	0 0994	Smooth, hard and mirror-like shining deposit Microcrystalline in structure.
	7	0 0035	0'0963	0'0996	Less shining. Uniform and hard deposit.
	10	0'0050	0 1010	0 1090	Hard but dull looking, crystalline in appear- ance.
Tellurium sol	5	0'00066	0'1096	0'1126	Deposit very shining and microcrystalline. Could take a high polish.
	10	0'00132	0'1096	0'1135	Deposit hard but less shining.
	15	0'00198	0'1207	0'1257	Deposit rough and cry- stalline. Optimum con- centration reached.
Tungsten trioxide sol	3	0'00020	0'1118	0'1158	Addition of colloid slightly improves the deposit, but copper sur- face is visible at places.
	5	0'00033	0'1155	0'1181	Deposit lustrous, hard and fine-grained.
	7	0'00047	0 1114	0 1144	Deposit less shining and crystalline. Optimum concentration reached.
Manganese dioxide sol	5	0'0375	0'1042	0'1051	Uniform, hard and mi- crocrystalline deposit.
	7	0'0525	0'0956	0'0958	Practically ideal deposit, close-grained, lustrous and hard.
	10	0'0750	0'1152	0'1169	Less shining and hard than with 7 c.c.

DISCUSSION.

From the above account it is proved beyond doubt that the addition of the colloids of the elements of groups VI and VII improves the deposit in brightness as well as in hardness; the only exception is sulphur, which being a non-metal, shows a different result. Iodine similarly in the next group, though gives quite a coherent deposit, lacks lusture completely. Another fact which this study reveals is that metallic colloids impart lustre to the nickel deposit, while oxide sols render the deposit very hard and uniform. Selenium, tellurium and molybdenum sols, in our opinion, will help the uniform and coherent deposition of nickel considerably. With molybdenum sol, the brightness is of such an order that a perfectly reflecting surface was obtained. Tungsten trioxide sol was the only one that gave a bright as well as a very hard deposit.

Further work on this problem is still proceeding in this laboratory.

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Received June 27, 1941

9-THIOLPHENANTHRENE AND SOME OF ITS DERIVATIVES

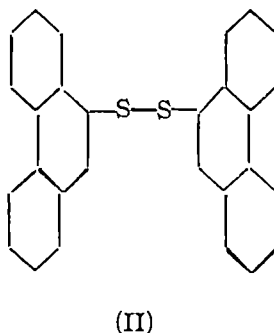
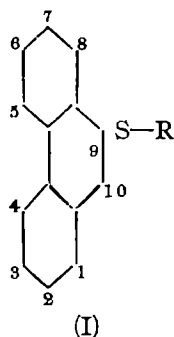
BY PARESH CHANDRA DUTTA.

9-Thiolphenanthrene and some of its derivatives are described.

Except 3-thiolphenanthrene, prepared by Field (*J. Chem. Soc.*, 1915, 117, 1214), the other thiolphenanthrenes are not known. The author was inclined to prepare the 9-thiol compound in the expectation of preparing some thioindigoid dyes which would be of interest on the relation between colour and chemical constitution. Werner and his collaborators (*Annalen*, 1915, 321, 248) have shown that by the action of concentrated sulphuric acid on phenanthrene, three mono-sulphonic acids—2, 3, and 9 are produced, but a good method for their separation was not worked out. Fieser (*J. Amer. Chem. Soc.*, 1929, 2460) later on has introduced a method by which these mono-sulphonic acids are obtained in better yield and in a more pure condition and incidentally he also discovered the presence of phenanthrene-1-sulphonic acid in these sulphonation products. 9-Thiolphenanthrene has been prepared from potassium-9-phenanthrene-sulphonate through sulphochloride and subsequent reduction, the potassium-9-phenanthrene-sulphonate having been prepared following Fieser's modified method (*loc. cit.*).

EXPERIMENTAL.

9-Thiolphenanthrene (I, R=H).



A mixture of potassium 9-phenanthrene-sulphonate (20 g.) and phosphorus pentachloride (25 g.) was treated with phosphorus oxychloride (5 c.c.) and heated to 140° for 1 hour under reflux and then the oxychloride

distilled off. The semi-solid mass was then left in contact with ice-water for a long time. The yellowish white solid was next filtered and thoroughly washed with water. The sulphochloride, thus obtained, was mixed with zinc dust (80 g.) and to the mixture sulphuric acid (120 c.c. diluted with 360 c.c. of water), was gradually added. When the reaction had slackened the mixture was heated on water-bath for about 5 hours with frequent shaking. On cooling, the mixture was filtered and the residue collected. The thiophenanthrene was then obtained from the residue by extraction with ether, drying the ethereal extract with fused calcium chloride and evaporation of ether. The thiol compound, thus obtained, was recrystallised from alcohol as white shining star-shaped crystals, m. p. 67° . It dissolves in sodium hydroxide solution with a light yellow colour but owing to oxidation the solution soon becomes turbid and the disulphide gradually separates out. (Found : S, 15.13. $C_{14}H_{10}S$ requires S, 15.24 per cent)

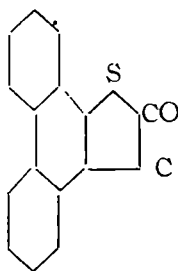
Phenanthrene-9-disulphide (II).—An alcoholic solution of iodine in slight excess was added to a solution of 9-thiophenanthrene (0.5 g.) in 59 c.c. of alcohol, when yellowish white crystals at once separated out which were warmed for some time under reflux. On cooling, the crystals deposited were filtered and recrystallised from alcohol as light yellow sphere-shaped crystals, shrinking at 137° and melting at 149° . (Found : S, 15.26. $C_{28}H_{18}S_2$ requires S, 15.31 per cent).

9-Acetylthiophenanthrene (I, $R=COMe$).—9-Thiophenanthrene (2 g.) was heated on a water-bath under reflux with acetyl chloride (6 c. c.) for 2 hours when the almost colourless liquid gradually became much darker. The product was then poured into water, sodium hydroxide solution was added to it and the alkaline solution extracted with ether. The ethereal extract was then dried with fused calcium chloride and the ether distilled off. The residue left behind was then recrystallised from petroleum ether in white needles which shrink at 80° and melt at 93° . (Found : S, 12.4 : $C_{16}H_{12}OS$ requires S, 12.7 per cent).

9-Benzoylthiophenanthrene, (I, $R=COPh$).—9-Thiophenanthrene (2 g.) was heated with benzoyl chloride (6 c.c.) in an oil-bath at 150° - 160° for 3 hours. The dark product was poured into water and treated with sodium hydroxide solution till alkaline. The alkaline solution was then extracted with ether, the ethereal extract dried and the ether distilled off. The residue was recrystallised from benzene in yellowish-white clusters of needles, which shrink at 95° and melt at 109° . (Found : S, 9.85. $C_{21}H_{14}OS$ requires S, 10.19 per cent).

9-Methylthiophenanthrene (I, R=Me).—9-Thiophenanthrene (2 g.) was dissolved in sodium hydroxide solution (5 c.c., 20%) and to this solution dimethyl sulphate was added gradually. The oily substance separating was extracted with ether, the ethereal extract dried with calcium chloride and the ether distilled off. The oil left behind after the distillation of ether gradually solidified forming long needle-shaped crystals, m. p, 75°. (Found : S, 13.91. $C_{15}H_{13}S$ requires S, 14.28 per cent).

9-Phenanthriathiophene-2': 3'-dione (III).



(III)

9-Thiophenanthrene (5 g.) was treated with oxalyl chloride (12 g.) and the mixture left at ordinary temperature for 24 hours. The excess of oxalyl chloride was distilled off and the residue after the addition of carbon disulphide (20 c.c.) was treated slowly with powdered anhydrous aluminium chloride (6 g.). The mixture was left at ordinary temperature for a short time and then refluxed for 1 hour. The carbon disulphide was then distilled off and the residue treated with crushed ice, filtered and washed. For purification, the residue was repeatedly extracted with dilute sodium carbonate solution and the substance obtained as a red precipitate by acidifying the reddish yellow alkali solution with hydrochloric acid. The substance was further purified by recrystallising from acetic acid in fine red needles. It shrinks at 227° and melts at 245°. Provisionally the substance is represented by the above formula. (Found : C, 72.56; H, 3.12. $C_{16}H_8O_2S$ requires C, 72.72; H, 3.03 per cent).

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Received July 3, 1941.



ON THE VELOCITY OF HYDRATION AND DEHYDRATION OF NICKEL SULPHATE.

By B. N. GHOSH.

A method has been developed by which it is possible to fix up the composition of the hydrates of inorganic salts by studying the velocity of their thermal dehydration under a fixed experimental condition. The process of hydration seems to be more complex and do not yield the above information.

The purpose of this note is to describe the technique of a method used for the measurement of the velocity of dehydration and hydration of some inorganic salts and also to present some results obtained, by which it has been found possible to fix up the composition of the hydrates of these salts. It has also been found that the rates of dehydration can be accelerated or retarded, and in some cases the temperature of decomposition of the hydrates lowered by the catalytic action of some finely divided metallic powders and salts. But the general feature of dehydration curve shows a number of breaks, with or without the presence of catalysts, whose position as regards composition of the hydrates remain unaltered by variations of the superincumbent pressure or by a variation of the temperature of dehydration, provided the latter be sufficiently high to decompose the hydrates whose composition is to be revealed. The present paper is however concerned with measurements on unadulterated and pure hydrated nickel sulphate, and though data have been obtained at 150° , 220° and 300° only, the figures for the last temperature are presented, as here all the features of dehydration are fully developed.

It is well known that anhydrous nickel sulphate can be prepared by heating the hydrated salt to dull redness (*vide* Mellor, "Treatise on Inorganic and Theoretical Chemistry", Vol. XV, p. 453). The anhydrous salt when crystallised from an aqueous solution at a low temperature contains seven molecules of water of hydration. When the usual physicochemical methods are adopted for determining the composition of the hydrates, it is found that stable molecules of the salt may exist in aqueous solution holding 1 to 7 molecules of water of hydration. It is also found that as the temperature of the salt is raised, more and more molecules of water of hydration are shaken off progressively up to a total number of six. The last molecule of water of hydration, which seems to be very tenacious, takes a longer time to go out, and persists up to 280° . After this it escapes on further heating.

Rakuzin and Brodsky (*Z. angew. Chem.*, 1927, **40**, 836) have studied the thermal dehydration of this salt. They find that it takes 5.5 hours of heating for obtaining a loss of weight corresponding to the escape of 4.5 molecules of water of hydration. The loss of weight with time has not, however, been studied by these authors in a quantitative way and so the formation of the hydrates can not be fixed from their measurements. An analogous paper on the hydration of anhydrous copper sulphate by Davis and Eyre (*Proc. Roy. Soc.*, 1923, **A104**, 512) shows that the absorption of moisture takes place in a series of discontinuous steps. Their curves representing the quantity of moisture gained as a function of time show that in the case of copper sulphate the segments of the curve are either straight lines or parabolas. But the points corresponding to the breaks do not show the existence of stable hydrates.

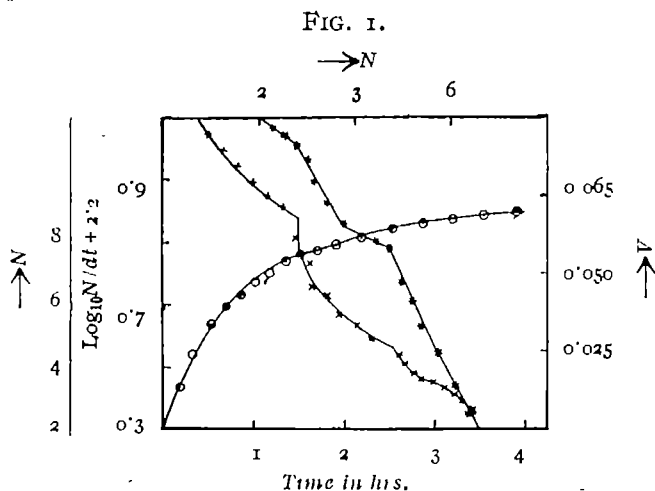
EXPERIMENTAL.

Of the various forms of apparatus used for analysing the above problem the one described below was found most useful and convenient. The container holding the salt was always in the form of a pyrex or metallic test-tube, the top of which was either closed or sealed. It was provided with a side-tube which was joined to a stop-cock. The latter in turn was connected with a U-tube containing P_2O_5 . The second arm of this U-tube was joined to a manometer and a pump by a flexible rubber tubing. The test-tube with its contents was put in a furnace at the desired temperature, and the pressure of the air over the salt was generally maintained at 2 cm. of Hg. Weights were taken every 10 minutes in the beginning and at longer intervals later on. In order to enable the test-tube and the salt to take up the experimental temperature quickly, after each weight has been taken, the former was temporarily put in a furnace at 600° , when generally within one minute the experimental temperature was obtained. Immediately after this the test-tube was transferred to the dehydrating furnace. Similarly to arrest the process of dehydration, when it was necessary to take weights at the end of a desired time, the test-tube was suddenly plunged in cold water to freeze the process. The equivalent correction to the time factor due to this pre-heating and post-cooling period was fixed up from a preliminary blank experiment. This inertial period was of course much less with the metallic vessel as compared with the glass one. It was also found convenient to mix about an equal weight of finely powdered glass with the salt which was also in the powdered form. This made the process of

dehydration more uniform as the crystals were kept separated from each other by the intervening glass fragments. The data for the initial portion of the curve was also obtained separately by taking several successive samples of the salt and determining their losses in weight after periods of heating lasting 10, 20 and 30 minutes., etc. Here the disturbing effects, which creep in the measurements of time when the weights are taken in several successive stages, vanish excepting for a common corrective addition to the heating time, which is necessary to bring the substance to the experimental temperature at the beginning of the experiment. Attempts were also made to take the weight of the samples with the help of a spring balance mounted in vacuum, but it was not found convenient. For the study of the rate of hydration, the cover of a test-tube holding the salt was removed and it was kept in a desiccator case (temp. = 32°) containing enough water to saturate the inside. Readings were taken at regular intervals as in the case of dehydration.

R E S U L T S.

The data obtained are shown on a simplified scheme by plotting ' N ', the number of molecules of water of hydration lost (in the case of dehydration), or gained (in the case of hydration) per molecule of NiSO_4 , as a function of the time, as in Fig. 1 (dehydration) or Fig. 2 (hydration). These points are marked in circles. In Fig. 1 $dN/dt \rightarrow N$ curve has been drawn marked with crosses and also $\log dN/dt \rightarrow N$, marked with stars. In the curves dN/dt has been represented as ' V ', the velocity of dehydration, expressed as the number of molecules of H_2O lost per molecule of NiSO_4 .



Two typical sets of observations are given in Tables I and II.

TABLE I.

M. W. of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} = 280.86$. N = Number of mol. of H_2O per mol. of NiSO_4 .

Time of heating.	Wt. of salt	Wt. lost.	N .	Time of heating.	Wt. of salt.	Wt. lost.	N .
0 min.	15.572 g.			80 min.	10.543 g	5.028 g.	5.031
10	14.461	1.110 g.	1.111	100	10.153	5.418	5.421
20	13.538	2.033	2.034	120	9.829	5.742	5.745
30	12.850	2.721	2.723	150	9.562	6.009	6.012
40	12.242	3.329	3.331	180	9.290	6.281	6.284
50	11.821	3.750	3.752	210	9.072	6.499	6.503
60	11.360	4.211	4.213	240	8.904	6.667	6.671

TABLE II.

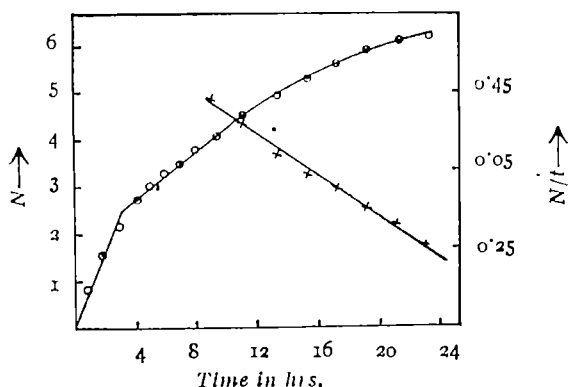
Duration of heating.	Wt. of salt Original.	Final.	Loss of wt.	N .	Duration of heating.	Wt. of salt Original.	Final.	Loss of wt.	N .
0.7 min.	7.215 g.	6.913 g.	0.302 g.	0.652	0.35 min.	7.082	5.664	1.551	3.412
0.15	7.045	6.535	0.680	1.505	0.45	7.223	5.354	1.861	4.014
0.25	7.471	6.016	1.199	2.500	0.55	7.148	5.148	2.067	4.504

DISCUSSION.

In the process of dehydration of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, three molecules of water of crystallisation escape within 40 minutes. Then the dehydration process slows down and the curve changes its nature at this transition point, corresponding to the formation of $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$. After two hours of heating, when the salt has the composition $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, the observational points shift to a third segment of the curve, where it is found that many molecules of nickel sulphate retain their last water of crystallisation even after prolonged heating for $5\frac{1}{2}$ hours. In the process of hydration of the anhydrous NiSO_4 at 32° the initial portion of the $N-t$ curve is almost straight, till 2.5 molecules of water of dehydration are absorbed per molecule of NiSO_4 . Then the points move to a second linear segment having a smaller slope. In the next stage, after 4 molecules of water of hydration have been absorbed per molecule of the anhydrous salt, the points lie on a para-

bolic curve $N=at-bt^2$ as has been shown in in Fig. 2 of $N/t-t$ where a perfect straight line has been obtained (points marked with crosses). The unit of N/t as represented, is the number of molecule of H_2O gained per hour

FIG. 2.



per molecule of $NiSO_4$. The last molecule of water of hydration seems to be absorbed in perceptible quantity only after 25 hours. The velocity of dehydration curve shows distinct breaks at values of ' N ' corresponding to 3, 5, and 6. This indicates the existence of hydrates having 4, 2, and 1 molecule of water of hydration. In order to see if the velocity of dehydration dies according to an exponential law, as is met with in radioactive transformation $\log dN/dt \rightarrow N$ graph is also drawn. It can be seen that the plottings can be grouped into 5 segments of which the first two are clear straight lines meeting at a sharp angle and the last three are approximately straight; but the position of the breaks on them also can be fixed up. There is no doubt that these breaks reveal the formation of hydrates having 1, 2, 3, 4, and 5 molecules of water of hydration.

AZINE DYES DERIVED FROM 9:10- PHENANTHRATHIOPHENE-2':3'-DIONE.

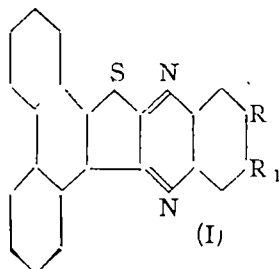
BY PARESH CHANDRA DUTTA AND RAMANI MOHAN SINHA.

Azine dyes derived from 9-phenanthrathiophene-2':3'-dione have been described.

9-Phenanthrathiophene-2':3'-dione, prepared from 9-thiolphenanthrene (*J. Indian Chem. Soc.*, 1941, **18**, 469, has been condensed with various *ortho*-diamines such as *o*-phenylenediamine, 2-chloro-4:5-toluenediamine, 2:3-diaminoquinoxalin, and 2:3-diaminophenazine and thereby the corresponding azines obtained. As has already been observed, the colour of these azine dyes deepens as the number of azine rings in the molecule increases. A further communication will describe the indigoid dyes derived from 9-thiolphenanthrene as well as 9-phenanthrathiophene-2':3'-dione. The work is in progress.

E X P E R I M E N T A L.

9: 10-*Phenanthrathiophene-phcnazine* (I, R = R₁ = H).

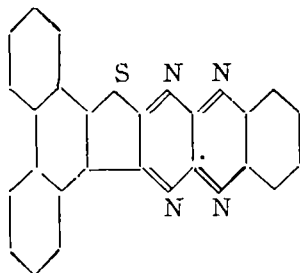


o-Phenylenediamine (2 g.) was added to a solution of 9-phenanthrathiophene 2': 3'-dione (I) (0.5 g.) in acetic acid (50 c.c.) and the solution shaken. The colour of the solution immediately became lighter and a yellow substance in the form of needles separated out. The mixture was boiled for 15 minutes more and filtered hot, the crystals washed with acetic acid and finally with water. The substance was then recrystallised from pyridine in yellow, slender shining needles, m. p. 255°. It dissolves in concentrated sulphuric acid with a green colour. (Found: N, 8.21. C₂₂H₁₂N₂S requires N, 8.33 per cent).

9: 10-*Phenanthrathiophene-2'-chloro-4':5'-tolazine* (I, R = Me; R₁ = Cl) was prepared in a similar way as the previous compound from 9-phenanthrathiophene-2': 3'-dione (0.5 g.) and 2-chloro-4: 5-toluenediamine (0.3 g.).

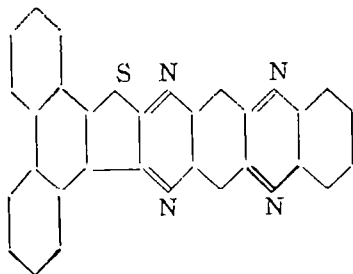
It was recrystallised from pyridine in yellow fine needles which shrink at 265° and melt at 271° . The compound dissolves in concentrated sulphuric acid with a blue colour. (Found : N, 7.02. $C_{23}H_{13}N_2ClS$ requires N, 7.28 per cent).

Quinoxaline-9: 10-phenanthrathiopheneazine..



It was prepared from 9-phenanthrathiophene-2': 3'-dione (0.3 g.) and 2: 3-diaminoquinoxalin (0.15 g.) in acetic acid solution by boiling for 2 hours. The solution was diluted, warmed and the brownish red precipitate collected. This was washed with dilute acetic acid and hot water and recrystallised from pyridine with the addition of hot water as a red crystalline mass, m. p. 233° - 34° . It dissolves in concentrated sulphuric acid with a violet colour. (Found : N, 14.14. $C_{24}H_{12}N_4S$ requires N, 14.43 per cent).

9 10-Phenanthrathiophene-phenazinezine,



It was prepared from 9-phenanthrathiophene-2': 3'-dione (0.3 g.) and diaminophenazine (0.2 g) in acetic acid solution by heating for 2 hours. The red solution during the process gradually became dark red and dark chocolate precipitate separated out. It was filtered and the precipitate washed with acetic acid and water. The dark-coloured precipitate was recrystallised from pyridine as a chocolate crystalline mass melting above 290° . It dissolves in concentrated sulphuric acid with a bluish black colour. (Found : N, 12.53. $C_{26}H_{14}N_4S$ requires N, 12.78 per cent).

STRUCTURE OF OXYMETHYLENE METHYL ETHYL KETONE AND OF OXYMETHYLENE METHYL- β -PHENYL ETHYL KETONE.

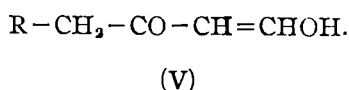
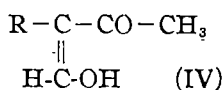
By S. N. JOSHI, R. KAUSHAL AND S. S. DESHPANDE.

By the reaction of self-condensation as also by condensation with cyanoacetamide it is shown that oxymethylene methyl ethyl ketone is $\text{CHOH}=\text{C}(\text{CH}_3)-\text{CO}-\text{CH}_3$ and oxymethylene methyl β -phenyl ethyl ketone is $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CO}-\text{CH}=\text{CHOH}$. The points of attack of formic ester on the ketone $\text{R}\cdot\text{CH}_2-\text{CO}\cdot\text{CH}_3$ are discussed.

By the action of formic ester on acetone Claisen (*Annalen*, 1894, 281, 309) obtained formyl acetone $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHO}$ (I) which according to him exists as the enol oxymethylene acetone $\text{CH}_3\cdot\text{CO}\cdot\text{CH}=\text{CHOH}$ (II), as it readily undergoes self-condensation to form triacetylbenzene (Claisen and Stylos, *Ber.*, 1888, 21, 1145).

Acetophenone similarly gives oxymethylene acetophenone which by self condensation gives tribenzoyl benzene.

In the case of the unsymmetrical ketone $\text{R}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ (III) formic ester can theoretically react at the methylene or the methyl group each of which is directly linked to the carbonyl and the resulting oxymethylene compound will be either (IV) or (V).



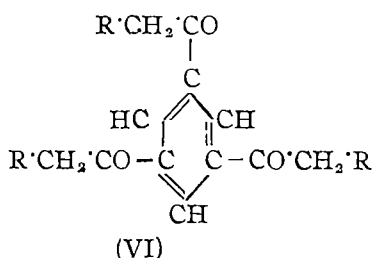
Although oxymethylene compounds have been prepared from some unsymmetrical ketones like (III) we found in the literature evidence which leads to the structure (IV) for some, while (V) for others. Thus Diel and Ilberg (*Ber.*, 1916, 49, 158) prepared the simplest member of the series, oxymethylene methyl ethyl ketone, by Claisen's method as also by the action of formaldehyde in aqueous solution on azobutanone. Since it gives with hydrazine 4:5-dimethylpyrazole they have given the oxymethylene compound the structure (IV, $\text{R}=\text{Me}$).

Benary, Meyer and Charisius (*Ber.*, 1926, 59, B, 108, 600) claim that the next homologue oxymethylene methyl propyl ketone is (V, $\text{R}=\text{Et}$) since it is transformed by ammonia into 5-butyryl-2-propyl-pyridine.

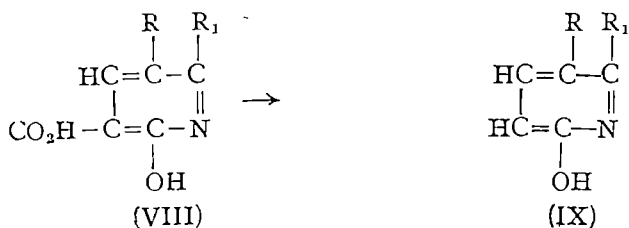
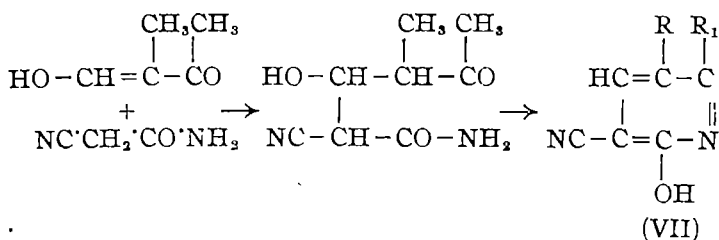
In view of such observations which indicate that oxymethylene methyl ethyl ketone is (IV, $\text{R}=\text{Me}$) but the higher homologue is (V, $\text{R}=\text{Et}$) we

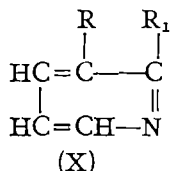
thought that it would be of some interest to bring forth some independent evidence bearing on this point. For this purpose we made use of two reactions namely (1) self condensation, such as that shown by oxymethylene acetone and oxymethylene acetophenone, and (2) condensation of these oxymethylene ketones (which are 1 : 3 dicarbonyl compounds and contain therefore a conjugated system) with cyanacetamide.

If a ketone produces the oxymethylene compound (V) three molecules of the latter condense to form the trisubstituted benzene (VI)



If, however, the oxymethylene compound is (IV) self-condensation is not possible. Barat (*J. Indian Chem. Soc.*, 1931, 8, 801) condensed oxymethylene acetophenone with cyanoacetamide and obtained 2-hydroxy-6-phenylpyridine. The condensation of cyanacetamide with oxymethylene methyl ethyl ketone, if the latter is (IV, R=Me) should give 2 : 3-dimethyl-5-cyano-6-oxypyridine (VII, R=R₁=Me) which after hydrolysis would yield the acid (VIII, R=R₁=Me). The latter on decarboxylation would give 2 : 3-dimethyl-6-oxypyridine (IX, R=R₁=Me) and finally after reduction 2 : 3-dimethylpyridine (X, R=R₁=Me).





If the oxymethylene compound is (V, R=Et) the final product of condensation with cyanoacetamide will be 2-ethylpyridine (X, R=H; R₁=Et). The final product was confirmed to be 2:3-dimethylpyridine and not its isomer 2-ethylpyridine.

In the matter of self-condensation reaction a striking contrast was observed between oxymethylene methyl ethyl ketone and oxymethylene acetone or oxymethylene acetophenone. The latter in alcoholic solution rapidly undergoes self-condensation and their titre against alkali progressively diminishes due to progressive disappearance of the enol.* Oxymethylene methyl ethyl ketone is a solid, melting at 73°. It could be distilled without decomposition at 250 mm. pressure, and the titre of alkali against a certain volume of its alcoholic solution remained constant over a period of one week. This lack of self-condensation supports the evidence obtained through cyanoacetamide condensation, namely oxymethylene methyl ethyl ketone is (IV, R=Me).

The oxymethylene compound from methyl β-phenylethyl ketone when subjected to the above tests showed an exactly opposite behaviour to that of oxymethylene methyl ethyl ketone. The former, therefore, seems to have the structure (V, R=Ph-CH₂). The titre of alkali required for a certain volume of its alcoholic solution gradually diminished and in the course of a week was roughly reduced to half. Condensation with cyanacetamide, if the oxymethylene compound is represented by (V), should give 2-(β-phenyl ethyl)-5-cyano-6-hydroxypyridine (VII, R=H; R₁=Ph·CH₂·CH₂-) which on hydrolysis should give the acid. The latter on decarboxylation should give 2-(β-phenyl ethyl) 6-hydroxy pyridine (IX, R=H; R₁=Ph·CH₂·CH₂) and finally 2 (β-phenyl ethyl)-pyridine (X, R=H; R₁=Ph·CH₂·CH₂) on reduction. If the oxymethylene ketone is, however, (IV) the final product of cyanoacetamide condensation should be 2-methyl-3-phenyl-methyl pyridine (X, R=PhCH₂; R₁=Me).

As the above two isomeric substituted pyridines have not been synthesised so far independently the proof of the structure of the final product of cyanoacetamide condensation was obtained by its oxidation.

* The reaction of self-condensation of these oxymethylene ketones judged from the alkali titre of the enol as also by estimation of its copper compound is found to be a trimolecular reaction (*unpublished work*).

(X, R=H, $R_1=Ph\cdot CH_2\cdot CH_2$) should give on oxidation benzoic acid and pyridine- α -carboxylic acid, while (X, R= $Ph\cdot CH_2$; $R_1=Me$) should give the $\alpha\beta$ -dicarboxylic acid. Actually benzoic acid and picolinic acid were obtained. The latter, however, could not be isolated and was analysed in the form of its characteristic copper salt.

EXPERIMENTAL

Oxymethylene methyl ethyl ketone (IV, R=Me) was prepared from methyl ethyl ketone (1 mol.), formic ester (1.5 mol.) and sodium (1 atom) in ether by Claisen's method. It distilled at $105^\circ-110^\circ/250$ mm, the distillate solidifying on cooling. The solid melts at 73° .

Condensation of the Oxymethylene ketone with Cyanacetamide. Formation of compound (VII, R= $R_1=Me$)—Cyanacetamide (11 g.) was dissolved in alcohol (90%) by warming such that it did not separate on cooling. Freshly prepared oxymethylene ketone (19 g.) was added and then finally 8 c.c. of piperidine. The mixture was refluxed on water-bath for 4 hours and the excess of alcohol was distilled off. The residual gum was rubbed with hydrochloric acid and the resulting semi-solid mass when rubbed with acetone became granular, yield 8 g.

It crystallised from alcohol in pale yellow needles, m.p. 270° . (Found : C, 64.6; H, 5.5; N, 19.2. $C_8H_8ON_2$ requires C, 64.8; H, 5.4; N, 18.9 per cent).

Formation of the Acid (VIII, R= $R_1=Me$).—The above cyano compound (5 g.) was heated in oil-bath at 150° for 2 hours with 30 c.c. of 50% sulphuric acid. The liquid on cooling was poured into water and the yellowish solid which separated was filtered, washed and dried. It was crystallised from glacial acetic acid in plates, which did not melt even up to 280° , yield almost theoretical. [Found : C, 57.5; H, 5.4; N, 8.2; Equiv., 166 (monobasic). $C_8H_8O_3N$ requires C, 57.49; H, 5.38; N, 8.38 per cent. Equiv., 167).

Decarboxylation of the Acid (VIII, R= $R_1=Me$): Formation of the hydroxy pyridine (IX, R= $R_1=Me$). The above acid (4 g.), mixed with a little copper powder, was distilled and the distillate solidified and weighed about 3 g. If crystallised from pyridine, m.p. 205° . (Found : C, 68.8; H, 7.2; N, 11.6. C_7H_8ON requires C, 68.3; H, 7.3; N, 11.4 per cent).

Reduction of the Hydroxy pyridine to 2:3-Dimethylpyridine.—The oxypyridine (IX, R= $R_1=Me$) (5.5 g.) was mixed with zinc dust (110 g.) and distilled in a current of dry hydrogen from a glass tube drawn out at

one end and heated in a small furnace. A yellowish liquid (3 g.) with pyridine-like odour was collected. This distilled at $160-61^{\circ}/710$ mm. (Found: N 12.7. C_7H_9N requires N, 13.1 per cent). The picrate melts at 181° and the chloroplatinate at 216° (decomp.). [Found: Pt, 31.06. $(C_7H_9N)_3PtCl_6H_2$ requires Pt, 31.25 per cent]. 2:3-Dimethylpyridine boils at $163-64^{\circ}/760$ mm. Its picrate and the chloroplatinate melt at 83° and 216° respectively. 2-Ethyl pyridine boils at $148-50^{\circ}/760$ mm. and its picrate and the chloroplatinate melt at $187-89^{\circ}$ and $165-67^{\circ}$ respectively. The identity of the base with 2:3-dimethyl pyridine was finally established by permanganate oxidation of the base to quinolinic acid whose melting point and the mixed melting point with a genuine specimen of quinolinic acid obtained from quinoline by oxidation was found to be 180° .

Oxymethylene Methyl- β -phenylethyl Ketone (V, $R=PhCH_2$) was prepared from benzylacetone, formic ester and sodium by Claisen's method. Benzylacetone was obtained from benzal acetone by reduction by sodium amalgam. Benzylacetone (10 g.) yielded about 11 g. of the crude oxymethylene ketone as a liquid. The latter distilled at $110-11^{\circ}/3$ mm. as a lemon-yellow liquid which solidified on colling. The oxymethylene ketone colours ferric chloride red and forms a copper salt which was crystallised from alcohol in plates, m.p. 176° (decomp.).

[Found: Cu, 15.7 ($C_{11}H_{11}O_2$)₂Cu requires Cu, 15.35 per cent]. Its anilide melts at 132° . (Found: N, 6.0. $C_{17}H_{17}ON$ requires N, 5.6 per cent).

The oxymethylene ketone began to change from light yellow to deep red and, due to the chemical change it was undergoing, it could not be purified. The titre of alkali against a certain volume of its alcoholic solution fell to nearly half during the course of one week.

Condensation of the Oxymethylene Ketone with Cyanoacetamide. Formation of 2- β -Phenylethyl -5-cyano-6-hydroxypyridine (VII, $R=H$; $R_1=Ph\cdot CH_2\cdot CH_2$).—This was effected as in the case of oxymethylene methyl ethyl ketone. The product was a semi-solid mass which was rubbed with ethyl acetate, filtered and the solid was washed with water to free it from unchanged cyanacetamide. 10 G. of the oxymethylene ketone yielded about 6 g. of the condensation product. It crystallises from alcohol in clusters of needles, m.p. 198° (decomp.). [Found: C, 74.4; H, 5.2; N, 13.1. $C_{14}H_{13}ON_2$ requires C, 75.0; H, 5.36; N, 12.5 per cent].

On hydrolysis in the manner described under methyl ethyl ketone the above condensation product gave an almost theoretical yield of the carboxylic acid. It crystallised from acetic acid in clusters of needles, m.p. $211-12^{\circ}$. (Found: C, 68.7; H, 5.3; Equiv., 241. $C_{14}H_{13}O_3N$ requires C, 69.1; H, 5.3 per cent. Equiv., 243).

On decarboxylation of the above acid the hydroxy pyridine (IX, $R=H$; $R_1=Ph-CH_2-CH_2$) distilled as a liquid which solidified on cooling. The solid crystallised from alcohol as thick small needles, m.p. 152° . (Found: C, 78.1; H, 6.3; N, 7.5. $C_{13}H_{13}ON$ requires C, 78.4; H, 6.5; N, 7.04 per cent).

When distilled with zinc dust in a current of hydrogen the above oxypyridine gave 2- β -phenylethyl pyridine (X, $R=Ph$; $R_1=Ph\cdot CH_2-CH_2$) which was obtained as a liquid with strong pyridine-like odour. It was purified by redistillation. (Found: C, 85.0; H, 7.1; N, 7.6. $C_{13}H_{13}N$ requires C, 85.2; H, 7.1; N, 7.65 per cent).

It forms a chloroplatinate which begins to blacken at 160° and melts at 185° .

Oxidation of 2- β Phenylethylpyridine.—The base (1.2 g.) was refluxed for 4 hours with a neutral 1.5% solution of potassium permanganate. On filtering, the clear filtrate was concentrated and acidified when a white solid separated. Crystallised from water it melted at 122° and was identified as benzoic acid from its melting point and its equivalent which was found to be 123.

The acid filtrate from benzoic acid was made exactly neutral by adding alkali and again concentrated. On adding cold concentrated solution of copper acetate the copper salt of picolinic acid came out as a shining blue crystalline solid. It was filtered, washed with water, dried, and analysed [Found: Cu, 18.6. Calc. for $(C_8H_4O_2N)_2Cu + 2H_2O$: Cu, 18.6 per cent].

THE ALKALOIDS OF *RAUWOLFIA CANESCENS*, LINN. PART II

BY (MISS) ASIMA MOOKERJEE.

Rauwolscine is hydrolysed by aqueous alkali to rauwolscinic acid, $C_{20}H_{24}O_3N_2$ which contains one CO_2H group. It can be reconverted into rauwolscine by esterification with methyl alcohol. Ethyl, *n*-propyl and *n*-butyl esters of rauwolscinic acid have also been described, as also some of their salts. The colour reactions of rauwolscinic acid are similar to those of the parent compound and yohimbine. The ultraviolet absorption spectra of rauwolscine and yohimbine have been found to be very similar

In a previous communication (*J. Indian Chem. Soc.*, 1941, 18, 33) the preliminary examination of a new alkaloid, rauwolscine ($C_{21}H_{26}O_3N_2$), isolated from *Rauwolfia Canescens*, has been reported. It was found to give colour reactions similar to those of yohimbine and was found to undergo hydrolysis by means of concentrated aqueous ammonia at room temperature to an acid, rauwolscinic acid. The same acid has now been obtained by hydrolysis of the alkaloid with aqueous potassium hydroxide in quantitative yield.

The acid forms pale yellow prisms, m. p. $262-64^\circ$ (decomp.), having $[\alpha]_D^{25} = +136.8^\circ$. It yielded a crystalline hydrochloride and a picrate. It can be esterified with methyl, ethyl, *n*-propyl and *n*-butyl alcohol. These esters are well defined crystalline compounds and form crystalline hydrochlorides. The analytical data of these esters and their salts support the formula, $C_{20}H_{24}O_3N_2$, previously suggested for rauwolscinic acid. The observed equivalent weight of this monobasic acid is also in good agreement with the above molecular formula.

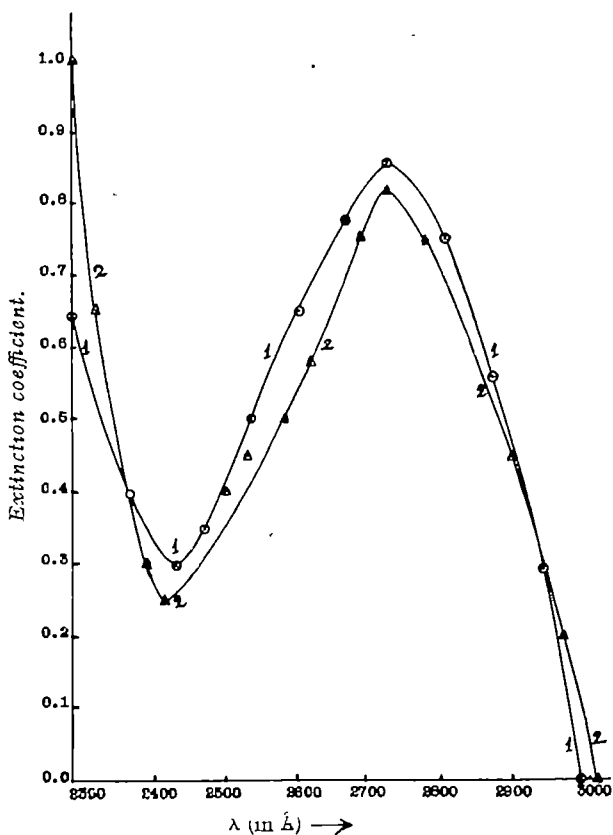
The colour reactions of rauwolscinic acid are very similar to those of rauwolscine or yohimbine, as will be evident from the following table.

Reagent.	Colour reactions of rauwolscinic acid.
Conc. H_2SO_4	Blue with a violet tinge, gradually fades away to pale green.
Conc. $H_2SO_4 + K_2Cr_2O_7$	Deep blue, then violet, finally purplish brown.
Erdmann's reagent	Purplish brown, then green and finally yellow.
Froehde's reagent	Indigo blue, gradually fades away to olive green, then greyish and finally dirty yellow
Mandelin's reagent	Olive green, quickly changing to brown, then reddish brown and finally purplish brown.

From the general chemical behaviour it was suggested in Part I that the main features of the structures of rauwolscine and yohimbine might prove to be very similar. Confirmation of this supposition is now available

from a comparison of the ultraviolet absorption spectra of the hydrochlorides of the two bases which are graphically represented in Fig. 1. Yohimbine hydrochloride (Merck) showed a well defined absorption band with the maxima at 2740\AA and a minima at 2430\AA . The corresponding figures for rauwolscline hydrochloride are 2750\AA and 2450\AA respectively.

FIG. 1



Absorption curves 1 and 2 refer respectively to hydrochlorides of yohimbine in water (dilution 1 in 20,000) and of Rauwolscline in water (dilution 1 in 27,000)

According to Karschulin (*Arch. Hemiju*, 1931, 5, 227) the absorption spectra of yohimbine and yohimbic acid are similar to those of indole but not to those of quinoline. One might consequently infer that rauwolscline contains an indole nucleus. This inference has already received independent support by the degradation of rauwolscline to an indole derivative which will be described in a subsequent communication.

E X P E R I M E N T A L.

Rauwolfscinic Acid.—When rauwolschine (0.5 g.) was heated on the water-bath with 10% aqueous potassium hydroxide (20 c.c.) for 4-5 hours, the base went into complete solution. The brownish yellow solution was filtered and the clear filtrate concentrated on the water-bath to about 15 c.c. Acidification with $N/2$ acetic acid (avoiding excess) precipitated rauwolfscinic acid, yield 86%. The product was twice crystallised from boiling water when pale yellow prisms, m. p. $262-64^{\circ}$ (decomp.) were obtained. The acid (0.254 g.) lost 0.0138 g. in weight when dried at $125-30^{\circ}$ for 4 hours in *vacuo* over P_2O_5 . [Found: H_2O , 5.43. $C_{20}H_{24}O_3N_2$, H_2O requires H_2O , 5.03 per cent. Found in dry specimen: C, 70.11; H, 7.22; Equiv.*, 349, 350. $C_{20}H_{24}O_3N_2$ requires C, 70.58; H, 7.06 per cent. Equiv. (monobasic), 340].

The substance is sparingly soluble in water and insoluble in alcohol, benzene, chloroform, ethyl acetate, ether and petroleum ether. 0.0590 G. of substance in 50 c.c. of water showed a rotation of $+0.13^{\circ}$ in 0.5 dcm. tube at 23° , whence $[\alpha]_D^{23} = +136.8^{\circ}$.

The *Hydrochloride of Rauwolfscinic Acid*.—The acid (0.15 g.) was dissolved in hot 2*N*-hydrochloric acid (5 c.c.). The star-shaped colourless crystals, which separated out on boiling, were recrystallised from hot water, m. p. $255.5^{\circ}-257.5^{\circ}$ (decomp.). (Found: Loss on drying at $120^{\circ}-25^{\circ}$ for $3\frac{1}{2}$ hrs. in *vacuo* over P_2O_5 , 11.2. $C_{20}H_{24}O_3N_2$, HCl , $2\frac{1}{2}H_2O$ requires H_2O , 10.7 per cent. Found in anhydrous specimen: Cl, 9.42. $C_{20}H_{24}O_3N_2$, HCl requires Cl, 9.43 per cent).

The *Picrate*.—An orange precipitate was obtained on treating an aqueous solution of the acid with aqueous picric acid. Crystallised from alcohol it formed shining brick-red plates, m. p. $232-34^{\circ}$ (decomp.). [Found in specimen dried† at $115-120^{\circ}$ for 4 hours in *vacuo* over P_2O_5 : N, 11.40. $C_{20}H_{24}O_3N_2$, $C_6H_2OH(NO_2)_3$, C_2H_5OH requires N, 11.38 per cent].

The *Ethyl Ester*.—A stream of dry hydrogen chloride was passed through a suspension of rauwolfscinic acid (0.25 g.) in absolute alcohol (10 c.c.) at 0° , till saturated. The acid gradually passed into solution and the clear solution on standing overnight deposited colourless shining needles of the ester hydrochloride, yield 0.26 g. The crystals were collected, washed with cold absolute alcohol and recrystallised from hot water, m. p. $262-64^{\circ}$ (decomp.). The substance did not suffer any loss on drying in *vacuo* over P_2O_5 for 3 hours at 120° . (Found: Cl, 8.84. $C_{22}H_{28}O_3N_2$, HCl requires Cl, 8.77 per cent).

* Excess of standard alkali was added to a known weight of the acid and titrated back rapidly with standard acid using phenolphthalein as indicator.

† No loss in weight was observed on drying.

The hydrochloride (0.07 g.) was dissolved in warm water (25 c.c.) and the solution was rapidly cooled and made just alkaline with ammonia. The shining, colourless needles, which were thus obtained, were washed with cold water and twice crystallised from ethyl alcohol when the ester melted at 234-36° (decomp.). Further crystallisations did not raise the m. p. The ester suffered no loss in weight when dried at 110°-15° for 4 hours in *vacuo* over P_2O_5 . (Found: C, 72.03; H, 7.47. $C_{22}H_{28}O_3N_2$ requires C, 71.74; H, 7.6 per cent).

The Picrate of the Ethyl Ester.—An orange precipitate was obtained on mixing ethereal solutions of the ester and picric acid. Crystallised from alcohol, it formed shining orange-yellow plates, m. p. 179.5°-181.5° (decomp.) [Found in specimen dried at 100°-105° for 3 hours in *vacuo* over P_2O_5 : N, 11.90. $C_{22}H_{28}O_3N_2$. $C_6H_2(OH)(NO_2)_3$ requires N, 11.72 per cent].

The n-Propyl Ester of Rauwolfscinic Acid—It was prepared in the same way as ethyl ester. The hydrochloride was purified by crystallisation from hot water when it formed colourless, slender needles, m.p. 264-66° (decomp.). It suffered no loss in weight when dried at 110-15° for 4 hours in *vacuo* over P_2O_5 . (Found: Cl, 8.56. $C_{23}H_{30}O_3N_2$, HCl requires Cl, 8.40 per cent).

The free base was liberated by the method followed in case of the ethyl ester, 0.16 g. of the hydrochloride requiring 50 c.c. water for complete solution. The shining silky rods of the *n*-propyl ester were crystallised from ethyl alcohol and had m. p. 206-8° (decomp.) (Found in specimen dried at 105-10° for 4 hours in *vacuo* over P_2O_5 : C, 72.06; H, 8.04. $C_{23}H_{30}O_3N_2$ requires C, 72.25; H, 7.85 per cent).

The n-Butyl Ester Hydrochloride of Rauwolfscinic Acid, prepared as usual, melted at 251-53° (decomp.). (Found in specimen dried at 120° for 4 hours in *vacuo* over P_2O_5 : Cl, 8.16. $C_{24}H_{32}O_3N_2$, HCl requires Cl, 8.2 per cent) The free base, *n*-butyl ester of rauwolfscinic acid, was prepared by the method described under the *n*-propyl ester. It formed pale, yellow shining needles (alcohol). It froths up at 105°-6° and melts at 181-182.5° (decomp.). (Found in specimen dried at 75-80° for 4 hours in *vacuo* over P_2O_5 : C, 72.44; H, 8.2. $C_{24}H_{32}O_3N_2$ requires C, 72.72; H, 8.09 per cent).

The picrates of the propyl and butyl esters could not be prepared.

The author desires to offer her best thanks to the University of Calcutta for the grant of a scholarship which has enabled her to carry out this investigation. Her best thanks are also due to Dr. P. K. Bose for his keen interest and for the facilities given, and to Mr. N. Ghosh, M.Sc. for the microanalyses.

ON THE MOVING BOUNDARY METHODS FOR THE DETERMINATION OF CATAPHORETIC SPEED OF COLLOIDS. PART II.

By N. C. SEN-GUPTA AND P. R. SINHA.

The suitability of the moving boundary method as developed by Mukherjee for the determination of cataphoretic speeds of concentrated colloids in which the electrical conductivity of the colloid particles is comparable with those of the intermicellary electrolytes has been discussed in the light of the electrolytic migration theory of Kohlrausch and Weber. This theory has been verified with mixtures of KCl and KIO_3 . The conditions necessary for reliable cataphoretic measurements have been experimentally secured with two ferric oxide and two aluminium oxide hydrosols and cataphoretic speeds generally reproducible within 2% have been obtained. The cataphoretic speeds of the same sols have been obtained by the transport apparatus of Engel and Pauli and the results are also reproducible within about 2%. The results of the moving boundary method have been found to agree with those of the transport method almost within the range of experimental accuracy.

In the determination of the cataphoretic velocity by the method of moving boundaries a colloid is regarded as a mixture of electrolytes, the colloidal micelles being assumed to be large polyvalent ions. A boundary is formed between the colloid and electrolytic solution, a constant current is passed and the rate of migration of the boundary is observed.

Mukherjee (*Proc. Roy. Soc.*, 1923, **A 102**, 103) developed a method by which the potential gradient at and behind the moving boundary can be measured across side-limbs fused with the main cataphoretic tube. He showed from direct measurements that unless the upper electrolyte is suitably chosen the moving boundary method is liable to give erroneous results.

Choice of the suitable upper electrolyte must rest on a knowledge of the type of colloid whose cataphoretic velocity is being measured. Three cases have got to be distinguished :

Case 1. The colloid contains an excess of dissolved electrolytes so that the contribution of the micelle ions to the conduction of current is very small.

Case 2. The conductivity of the micelle ions is comparable with those of the intermicellary electrolytes.

Case 3. The colloid contains very little dissolved electrolyte except the "gegenion."

In the case of colloids of the first kind, the upper electrolyte should have the same composition as that of the intermicellary electrolyte and should be equiconducting with the colloid. This case has been dealt with in Part I (Sen-Gupta, *J. Indian Chem. Soc.*, 1938, **15**, 483) where it has been shown that under proper conditions moving boundary and microscopic methods give identical results.

In the case of colloids of the second kind, it is not possible to determine without actual measurements the composition of the suitable upper liquid with which the colloid will move unchanged. This has got to be obtained by trial and Mukherjee's cataphoretic tube appears to be a very convenient apparatus for such measurements.

The theory of the moving boundary method for colloids of the second kind, which rests on the relation of Kohlrausch (*Ann. Physik.*, 1897, **62**, 209) and Weber (*Sitzungsber. Berlin Akad.*, 1897, 936) for constant ionic migration has been recently reviewed by several workers (Henry and Brittain, *Trans. Faraday Soc.*, 1933, **29**, 798; Komagata, *Tokyo Electrotech. Lab. Japan*, 1933, No. 348; Hacker, *Koll.-Chem. Beih.*, 1935, **41**, 147). Of these the work of Hacker deserves a special attention. He used Mukherjee's cataphoretic tube and showed that the relation of Kohlrausch and Weber holds good for mixtures of electrolytes. He also found experimentally, in the case of a ferric oxide sol, the suitable upper electrolyte with which the colloid moves unchanged. He, however, did not compare his results with those obtained by other methods. This appears desirable.

The case of colloids of the third kind corresponds with the solution of a single electrolyte and is comparatively simple. Its study is also expected to give some useful information. This will be dealt with in future.

In the present communication the suitability of the moving boundary method for (i) mixtures of potassium chloride and potassium iodate, (ii) two ferric oxide hydrosols and (iii) two aluminium oxide hydrosols has been studied and the results have been compared with those obtained by the transport method as developed by Engel and Pauli (*Z. physikal. Chem.*, 1927, **126**, 247).

EXPERIMENTAL.

Moving Boundary Method.

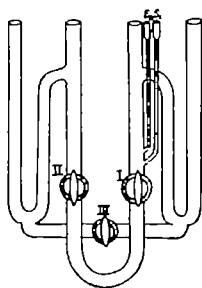


FIG. 1.

Moving boundary apparatus.

Cataphoretic measurements have been carried out with a U-tube, in which two wide stop-cocks, having the same bore as that of the cataphoretic tube, have been fused in the body of the tube. The apparatus is shown in Fig. 1. This apparatus is specially suitable for colourless solutions.

The tube is filled with the colloid up to the stop-cocks I and II*. The stop-cocks are then closed and the top portion is filled with the suitable covering electrolyte, stop-cock III being kept open. The tube is then immersed in the thermostat, and stop-cock II is opened. After half an hour stop-cock I is opened and III closed. Current is allowed to flow in the proper direction and potential measurements taken at definite intervals between the side tubes S_1 and S_2 . The measured potential remains at first constant, then rises as the boundary enters into the region between S_1 and S_2 and finally assumes a higher constant value as the boundary passes up the side tubes. The speed of the boundary, when it is between the side-tubes, is observed with a cathetometer and a stop-watch. Current is kept constant by means of a hand regulated rheostat.

The method of calculating the cataphoretic speed and specific conductivity behind the boundary has been detailed previously (Sen-Gupta, *J. Indian. Chem. Soc.*, 1937, **14**, 685).

Transport Method.

In the transport method the amount of colloid passing through any particular cross section of the solvent due to the passage of a definite quantity of electricity is analytically estimated. Besides the difficulties of analytical estimation the following two objections may be raised against the ordinary method**.

(a) Electrodes being directly immersed in the colloid polarisation occurs *e.g.*, in Paine's method (*Trans. Faraday Soc.*, 1928, **24**, 412) and,

(b) During electrolysis colloid in one region of the tube is diluted and in another region concentrated producing a corresponding mixing.

These two objections have been eliminated in the method of Eigel and Pauli (*loc. cit.*). Further, the analysis of unnecessarily large amount of colloids is avoided. The apparatus (Fig. 2) is really an extension of the moving boundary apparatus with this difference that the plane of

* The density of colloidal solutions is generally greater than that of the electrolytes which are adjusted with the colloids so that the electrolyte solutions are generally placed above the colloids.

** Mukherjee (*Kolloid Z.*, 1935, **72**, 178) pointed out another source of error which sets a limit to the wide applicability of the transport method. This trouble comes in when the intermicellary electrolyte contains an excess of the ion present in the colloid and when the velocity of the ion is markedly different from that of the colloid.

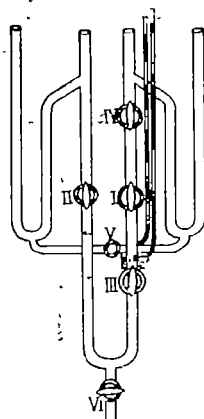


FIG. 2.

Transport apparatus
(Engel and Pauli)

reference is placed well below the boundary and thus the troubles occurring at the boundary do not enter into the results. The apparatus of Engel and Pauli without any modification has been used in the present investigation. The working of the apparatus has been described by Engel and Pauli. The colloid is originally filled up to the stop-cocks I and II and after passing the current the amount of colloid in the region between III and IV is analysed. The cataphoretic speed is calculated by the formula

$$C.V. = \frac{(a/c - \phi)k_0}{i \cdot t}$$

where a is the amount of colloid in g. found in the region between stop-cocks III and IV, c , the concentration of the colloid in g. per c.c., ϕ , the volume in c.c. between stop-cocks I and III, k_0 , the specific conductivity of the colloid, i , the current strength and t , the time of electrolysis.

Equiconducting solutions of potassium chloride have generally been used as the upper electrolyte. The specific conductivity of the sol has been measured *in situ* by the conductivity electrodes EE' before and after passing the current. If the conductivities are different, this shows that the disturbances at the boundary have entered into the colloid down to the plane of reference. Such measurements are rejected.

Preparation of Sols.—Ferric oxide hydrosol A was prepared by the prolonged dialysis of a concentrated solution of FeCl_3 , partially neutralised with NH_4OH . The sol has been allowed to age for about one year.

Ferric oxide hydrosol B was prepared by the precipitation of hydrated Fe_2O_3 from a concentrated solution of FeCl_3 with NH_4OH . The precipitate was washed repeatedly with distilled water on a Buchner funnel and then peptised with the least amount of FeCl_3 . The resulting sol was dialysed for fifteen days with occasional change of distilled water and then allowed to age at 70° for twelve hours.

Aluminium oxide hydrosol A was prepared in the same way as ferric oxide hydrosol B and the sol allowed to age for one month at the room temperature.

Aluminium oxide hydrosol B was obtained by the electrodialysis of sol A in a three-chambered electrodialyser with occasional change of

water. With the progress of electrodialysis gelatinous precipitate was found to be thrown down. In order that the sol might not become too dilute, electrodialysis was stopped after three days. The sol was allowed to age for one month at the room temperature.

Analysis of the Sols.—Ferric oxide hydrosols were dissolved in hydrochloric acid and concentration of iron estimated by dichromate titration using diphenylamine.

Aluminium oxide hydrosols were also dissolved in concentrated hydrochloric acid and concentration of aluminium estimated by the 8-oxyquinoline method (Berg, *Z. anal. Chem.*, 1927, **71**, 369).

Hydrogen Ion Concentration.— p_H has been measured with quinhydrone and glass electrodes McClatche (*J. Phys. Chem.*, 1932, **36**, 2087) showed that the p_H of ferric oxide hydrosols could be estimated equally well by means of the quinhydrone and the glass electrodes, while hydrogen electrode gave erratic results. The same has also been observed in this investigation.

Chlorine Ion Concentration and Total Chlorine.—Chlorine ion concentration has been measured by means of silver-silver chloride electrodes, prepared by the method of Noyes and Ellis (*J. Amer. Chem. Soc.*, 1917, **39**, 2534) and total chlorine estimated by means of volumetric titrations with standard solutions of silver nitrate after dissolving the colloid in nitric acid.

Both conductivity and p_H of freshly prepared sols have been found to change at first rapidly with time and finally become almost constant. The values of the conductivities and p_H of the sols have not measurably changed during the period of measurements.

Methods of measuring current strength, and potential gradient have been described previously (Sen-Gupta, *loc. cit.*).

RESULTS.

Composition. Compositions of the sols and of the ultrafiltrates are shown in Tables I and II. The ultrafiltrates of ferric oxide hydrosols contain negligible quantity of iron. Similar results have also been obtained recently by Kargin and Kiseleva* (*J. Phys. Chem. Russ.*, 1938, **11**, 461).

The conductivity of the micelle ions can be calculated from the above tables assuming that the mobility of the electrolytic ions in the colloid and

* Absorption spectra of ferric oxide hydrosol was unaffected by the addition of $K_4Fe(CN)_6$ or KCNS showing absence of any ferric ion.

TABLE I.

System.	Total iron as Fe_2O_3 .	p_{H} .	Chlorine ion activity.	Total chlorine.	Specific condy. at 35° (mhos)
Ferric oxide hydrosol A	1.987%	3.37	$3.27 \times 10^{-1}N$	$43.6 \times 10^{-4}N$	$69.53 \times 10^{-}$
Ultrafiltrate of above	Negligible	3.09	...	1.24	52.30
Ferric oxide hydrosol B	1.471%	3.29	2.06	25.6	44.1
Ultrafiltrate of above	Negligible	3.09	...	0.95	27.3

TABLE II.

System.	Total aluminium as Al_2O_3 .	p_{H} .	Chlorine ion activity.	Total chlorine.	Specific condy. at 35° (mhos)
Aluminium oxide hydro- sol A	1.271%	4.11	$2.30 \times 10^{-3}N$	$2.54 \times 10^{-4}N$	135.6×10^{-3}
Ultrafiltrate of above	0.0261	4.06	...	1.25×10^{-3}	64.02
Aluminium oxide hydro- sol B.	0.654	5.10	3.3×10^{-4}	8.9×10^{-4}	4.28
Ultrafiltrate of above	0.0057	4.67	.	3.0×10^{-4}	3.81

in true solutions at same concentrations are equal. From the activities of Cl-ion and H-ion in Table I, the specific conductivity of ferric oxide hydrosol A due to the intermicellary electrolyte is

$$400 \times 4.3 \times 10^{-7} \text{ mho} + 90 \times 3.27 \times 10^{-6} \text{ mho} = 46.6 \times 10^{-5} \text{ mho.}$$

where 400 is the mobility of H-ion in a $10^{-1}N$ solution at 35°, 90, the same for Cl-ion at $10^{-3}N$ solution (Davis, "Conductivity of Solution," 2nd Ed. p. 205) and 4.3×10^{-7} and 3.27×10^{-6} are respectively the concentrations of H-ion and Cl-ion in g. equivalent per c.c. (see Table I). Thus the specific conductivity due to the micelle ion is $22.9 \times 10^{-5} \text{ mho}$ ($69.5 \times 10^{-5} \text{ mho} - 46.6 \times 10^{-5} \text{ mho}$). This can also be calculated in another way. The equivalent concentration of the micelle ion may be assumed to be given by the difference of a_{Cl} and a_{H} and equals $2.84 \times 10^{-3}N$. The mobility of the micelle ion ($C. V. \times F$) is about 57.6 (see Table XV) so that the specific conductivity due to the micelle ion equals $15.8 \times 10^{-5} \text{ mho}$. In view of the simplifying assumptions involved in these calculations a close agreement between the two results is not

expected. It is, however, evident from the above that the specific conductivity of the micelle ions is comparable with that of the intermicellary electrolytes.

Reproducibility of Measurements.

The reproducibilities in the measurements of potentials and cataphoretic speeds are shown in Table III, IV and V.

Since the movement of the boundary has been generally followed over a length of 1 cm. and the boundary could be read to within 0.05 mm., a reproducibility of more than $\pm 0.5\%$ is not expected. The reproducibility is generally within 2% except in the case of aluminum oxide hydrosol A using KCl as the upper liquid. Equiconducting KCl solution is, however, not a suitable upper liquid for aluminium oxide hydrosols. The reproducibility is also not so good with aluminium oxide hydrosol B. In the measurement of specific conductivity of the sol behind the boundary the results are reproducible within 1%.

Measurement of Potential gradient in the Sol layer behind the Moving Boundary.

TABLE III.

Temp. = $35^\circ \pm 0.05^\circ$. Fe_2O_3 sol A (sp. conductivity = 69.53×10^{-5} mho)

Upper liquid HCl (sp. conductivity = 69.50×10^{-5} mho).

T = time in sec. P = potential in volts.

T	...	0	120	360	570	720	1080	1380	1860	2160	2280	2460	2700
P	...	2.937	2.909	2.906	2.906	2.962	3.445	3.897	4.651	5.02	5.085	5.122	5.1

Specific conductivity of the sol layer behind the boundary

$$= \frac{2.906}{5.122} \times 69.5 \times 10^{-5} \text{ mho} = 39.45 \times 10^{-5} \text{ mho.}$$

TABLE IV.

Temp. = $35^\circ \pm 0.05^\circ$. Al_2O_3 sol A (sp. conductivity = 135.6×10^{-5} mho).

Upper liquid = equiconducting KCl.

Time (sec.)	...	0	480	840	1140	1440	1680	2040	2160	2280	2460
Potential (volt)		5.195	5.260	5.715	6.17	6.74	7.075	7.50	7.525	7.65	7.65

Sp. conductivity of the sol behind the boundary

$$= \frac{5.195}{7.650} \times 135.6 \times 10^{-5} \text{ mho} = 92.1 \times 10^{-5} \text{ mho} = 92.1 \times 10^{-5} \text{ mho.}$$

Reproducibility of Cataphoretic Velocity Measurements.

TABLE V.

Temp. = $35^{\circ} \pm 0.05^{\circ}$

Fe ₂ O ₃ Hydrosol A			Al ₂ O ₃ Hydrosol A		
(Sp. condy. = 69.53×10^{-3} mho).			(Sp. condy. = 135.6×10^{-3} mho).		
Upper liquid = Hydrochloric acid			Upper liquid = AlCl ₃ solution (Sp.		
(Sp. condy. = 141.6×10^{-3} mho).			condy. = 137.2×10^{-3} mho).		
Specific condy. of the sol. behind the			Sp. condy. behind the boundary		
boundary = 57.24×10^{-5} mho.			= 136.0×10^{-3} mho.		
Time.	Distance.	C.V. (cm./sec.)	Time.	Distance.	C.V. cm./sec.
409 sec	0.5 cm.	57.2×10^{-5}	211 sec.	0.3 cm.	59.7×10^{-5}
810	1.0	58.3	405	0.685	60.6
972	1.2	58.3	620	0.985	60.0

Mixed Electrolytes.

The results of the measurements with mixed electrolytes are given in Table VI.

TABLE VI.

Temp. = $35^{\circ} \pm 0.05^{\circ}$. Upper electrolyte = 0.02N-KCl (sp conductivity = 33.12×10^{-4} mho).

Indicator composition	Sp condy. (mho).	Sp condy. behind the boundary from potential measurements. (mho).	V_{IO_3} (cm./sec.)
0.02N-KIO ₃	24.6×10^{-4}	16.6×10^{-4}	43.2×10^{-5}
		16.3	42.5
0.0133N-KIO ₃	27.4	20.6	42.8
0.0067N-KCl		20.1	41.5
0.0067N-KIO ₃	30.3	25.9	42.4
0.0133N-KCl		25.6	41.4

Velocity of iodate ion has been calculated by the relation,

$$V_{IO_3} = \frac{V_{Cl} \cdot K_{KIO_3}}{K^1 K_0 / K - K_{KCl}}$$

where K , K_0 and K^1 denote respectively the specific conductivity of the indicator behind the boundary, of the original indicator solution, and of the KCl layer, and K_{KCl} and K_{KIO_3} the partial conductivities of the two electrolytes in the mixture and V_{Cl} and V_{IO_3} the absolute velocities of Cl-ion and IO₃-ion respectively. V_{Cl} has been put equal to 86.3×10^{-5} cm/sec. at 35°

and at 0.02N concentration (Sen-Gupta and Mittra, *J. Indian Chem. Soc.*, 1937, **14**, 645). Values for K_{KCl} and K_{KIO_3} have been obtained by dividing the equivalent conductivities at 0.02N strength by the corresponding concentration in the mixture. Since the ionic strength of the indicator has been kept constant at 0.02N, this gives the true partial conductivities of the electrolytes. Values for V_{IO_3} thus obtained have been given in the fourth column of Table VI.

V_{IO_3} calculated from the specific conductivity and the transport number at 0.02N concentration at 35° ($T_{10_3}=0.336$) and is found to be 42.8×10^{-5} cm/sec. The observed and calculated values for the velocity of iodate ion are in good agreement.

Ferric Oxide Hydrosol.

In Tables VII and VIII are given the results of measurements with ferric oxide hydrosols A and B. Hydrochloric acid of different concentrations has been used as the upper liquid. It follows from theoretical con-

TABLE VII.

Temp. 35° ± 0.05°.

Ferric oxide hydrosol A (Sp. condy. = 69.53×10^{-5} mho).			Ferric oxide hydrosol B (Sp. condy. = 44.1×10^{-5} mho).		
Specific conductivity of upper liquid (HCl) (mho)	sol following the *boundary (mho).	C.V. (cm/sec.).	Specific conductivity of upper liquid (HCl) (mho)	sol following the *boundary (mho).	C.V. (cm/sec.).
69.53×10^{-5}	38.74×10^{-6}	68.4×10^{-5} 69.5 66.3	48.28×10^{-5}	25.54×10^{-5}	64.6×10^{-5} 61.4
			48.28	25.37	61.1
69.53	39.45	66.7 66.8			62.6 64.4
141.6	57.24	57.2 58.3 58.3	78.92	33.63	60.9 60.3 60.5
163.1	64.22	57.7 57.6 57.2	114.3	39.20	54.9 56.2
			155.5	43.98	51.9
188.7	72.02	57.7 57.7 57.9			51.7
			155.5	43.83	51.7 52.0
			158.6	44.16	50.0 51.1
			168.7	47.00	50.8 52.1

* From potential measurements.

siderations that only rising boundaries should remain sharp. This has actually been found to be the case. The concentration of hydrochloric acid has been experimentally found for which the conductivity of the sol layer following the boundary is approximately the same as that of the original sol. This represents the ideal condition according to the relation of Kohlrausch and Weber. The measured cataphoretic velocity at this region does not change with slight alteration in the specific conductivity of the upper liquid. The results also correspond with the values obtained by the transport method.

With ferric oxide hydrosol B moving boundary measurements have also been carried out with (a) ultrafiltrate and (b) mixtures of HCl and FeCl_3 solutions as the leading electrolyte. It has been found that the measured cataphoretic speeds change with the specific conductivities of the FeCl_3 and HCl mixtures.

TABLE VIII.

Temp. = $35^\circ \pm 0.05^\circ$.

Ferric oxide hydrosol B.

Upper electrolyte.	Specific conductivity of upper electrolyte. sol following the boundary *		C.V. (cm/sec.)
Ultrafiltrate of the sol	27.26×10^{-5} (mho.)	22.16×10^{-5} (mho.)	63.9×10^{-5} 66.4
Mixture of FeCl_3 and HCl $p_H = 3.21$	45.0	30.18	63.7 63.9
Mixture of FeCl_3 and HCl $p_H = 3.15$	97.12	48.45	56.6 57.1
Mixture of FeCl_3 and HCl $p_H = 3.14$	143.8	56.5	46.8 47.2

* From potential measurements.

Aluminium Oxide Hydrosol.

In Table IX results of measurements with aluminium oxide hydrosols A and B have been recorded.

Aluminium oxide hydrosol A has a specific conductivity of 135.6×10^{-5} mho. An equiconducting solution of AlCl_3 has the same p_H as that of the sol namely 4.11. Further the cataphoretic speed of the particles is nearly the same as that of Al^{3+} ion in the equiconducting solution. These con-

siderations show that the equiconducting AlCl_3 solution should serve the purpose of the upper electrolyte. Measurements have been carried out with an equiconducting KCl solution for comparison. The specific conductivity of the sol behind the boundary is much less in the latter case and the observed cataphoretic speeds are also lower.

With aluminium oxide hydrosol B different solutions of AlCl_3 have been tried until one is found for which the specific conductivity of the sol behind the boundary is the same as that of the original sol. Both the rising and falling boundaries remained sharp in this case. Theoretical considerations, however, show that only rising boundaries give the true cataphoretic speeds.

TABLE IX.

Temp. $35^\circ \pm 0.05^\circ$.

Al_2O_3 Hydrosol A (sp. condy. 135.6×10^{-5} mho).			Al_2O_3 Hydrosol B (sp. condy. $= 4.28 \times 10^{-5}$ mho).			
Specific conductivity of upper electrolyte (mho).	sol following the boundary* (mho).	C V. (cm/sec)	Specific conductivity of upper electrolyte (mho) (AlCl_3).	sol following the boundary* (mho).	C V (cm/sec.) Falling Rising boundary. boundary	
KCl— 135.4×10^{-6}	99.6×10^{-6}	54.6×10^{-5}	4.28×10^{-5}	3.71×10^{-5}	49.5×10^{-5}	—
		52.5			49.2	
		55.7			46.9	
KCl— 135.4	101.3	53.7	4.36	3.71	45.1	53.5×10^{-5}
		52.8			44.1	54.6
		54.3	5.00	4.26	44.6	50.8
AlCl_3 —137.2	136.0	59.7			47.3	54.1
		60.7	5.50	4.51	47.3	55.0
		60.0			43.9	53.8

* From potential measurements.

Transport Method.

The apparatus was calibrated with 0.1N-KIO₃. The results of three independent measurements are shown in Table X.

TABLE X.

Temp. $35^\circ \pm 0.05^\circ$.

$M/10$ -KIO₃ soln. Upper electrolyte = $M/10$ -KCl soln. $\phi = 5.602$ c.c.

Time of passing the current.	Current (amp).	KIO ₃ soln. transported	T_{IO_3} .
3600 sec.	10.74×10^{-3}	1.33 c.c.	0.332
3600	13.02	1.60	0.330
3420	13.50	1.58	0.330

Transport number of IO_3^- ion in KIO_3 at 35° and at the dilution $0.1N$ can be calculated from the mobility data at 18° and from the transport number equation of Onsager and comes out to be 0.326.

The results of measurements with ferric oxide hydrosol A and B and aluminium oxide hydrosol A and B are shown in Tables XI–XIV. The results in the transport method are independent of the specific conductivity of the upper electrolyte as has been shown with ferric oxide hydrosol B:

TABLE XI

Temp. = $35^\circ \pm 0.05^\circ$. Ferric oxide hydrosol A (sp. condy. = 69.53×10^{-5} mho).
Upper electrolyte = KCl (sp. condy. = 69.50×10^{-5} mho.).

Time of passing the current.	Current (amp.).	Sol. transported.	C.V. (cm/sec.)
2700 sec.	49.7×10^{-5}	1.07 c.c.	55.5×10^{-5}
2400	57.7	1.146	57.4

TABLE XII.

Temp. = $35^\circ \pm 0.05^\circ$. Ferric oxide hydrosol B (sp. condy. = 44.1×10^{-5} mho).
Upper liquid = HCl.

Sp. condy. of upper electrolyte in mho.	Time of passing the current.	Current in amp.	Sol transported.	C.V. (cm/sec.)
60.16×10^{-5}	2400 sec.	50.57×10^{-5}	1.441 c.c.	52.3×10^{-5}
78.92	2400	60.10	1.688	51.5
73.4	2400	54.94	1.537	51.3

TABLE XIII.

Temp. = $35^\circ \pm 0.05^\circ$. Aluminium oxide hydrosol A (sp. condy. = 135.6×10^{-5} mho). Upper electrolyte = KCl solution (sp. condy. = 135.4×10^{-5} mho).

Time of passing the current.	Current (amp.).	Sol transported.	C.V. (cm/sec.)
3600 sec.	91.27×10^{-5}	1.41 c.c.	58.1×10^{-5}
3600	121.4	1.83	57.7

TABLE XIV.

Temp. = $35^{\circ} \pm 0.05^{\circ}$. Aluminium oxide hydrosol B (sp. condy = 4.28×10^{-5} mho) Upper electrolyte = KCl (sp. condy.) 4.26×10^{-5} mho).

Time of passing the current.	Current (amp.).	Sol transported	C.V. (cm/sec.)
2700 sec.	36.0×10^{-8}	1.152 c.c.	50.4×10^{-6}
2700	41.4	1.319	50.5

The results of measurements by the transport method have been compared with those obtained by the moving boundary method in Table XV. The agreement is very close and generally within the range of experimental accuracy.

TABLE XV.

Temp. = $35^{\circ} \pm 0.05^{\circ}$.

Sol.	C.V. (cm/sec.) obtained by moving boundary method.	C.V. (cm/sec.) obtained by transport method
Fe_2O_3 Sol A	57.6×10^{-6}	56.5×10^{-6}
Fe_2O_3 Sol B	51.4	51.7
Al_2O_3 Sol A	60.1	57.9
Al_2O_3 Sol B	52.5	50.4

CONCLUSION.

The results indicate that for concentrated colloids the moving boundary method is as suitable as the transport method. The suitability of the moving boundary method, however, depends on the direct determination of the potential gradient of the sol layer behind the boundary besides the rate of migration of the latter. If one tries to calculate the cataphoretic speed from the specific conductivity of the leading electrolyte the result becomes two to three times greater.

In the procedure of Kruyt and Willigen (*Kolloid Z.*, 1928, **44**, 22) the cataphoretic speed with the rising boundary is calculated from the speed of the boundary and the potential gradient in the upper electrolyte (ultrafiltrate) and the cataphoretic speed with the falling boundary from the speed of the boundary and the potential gradient in the sol layer. The mean of the two is assumed to represent the true cataphoretic speed.

With concentrated colloids, however, it is not generally possible to get both the boundaries sharp.

Thus it may be stated that an accurate determination of the cataphoretic speed of concentrated colloids rests on (a) the proper choice of the upper electrolyte and (b) the direct determination of the potential gradient or specific conductivity of the indicator solution behind the boundary.

The transport method is comparatively free from such troubles. If, however, the intermicellary electrolyte contains an excess of the ion present in the colloid (*e g.* Al-ion in aluminium oxide hydrosol) and if the mobility of the ion is markedly different from that of the colloid then the transport method becomes unsuitable. In the present investigation with the aluminium oxide hydrosols the concentration of Al-ion : total Al in the colloid was less than 1 : 50 as estimated by means of ultrafiltration. Further, the mobility of Al-ion is almost the same as that of the colloid. Thus the error introduced due to the presence of Al-ion is negligible.

Our best thanks are due to Prof. J. N. Mukherjee, D.Sc., for his suggestions and kind interest in the work and to the University of Calcutta for laboratory facilities.

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Received June 10, 1941.

REACTION BETWEEN GLUCOSE AND IODINE IN ALKALINE MEDIUM. EFFECT OF NEUTRAL SALTS.

BY KESHO DASS JAIN AND B. L. VAISH.

The iodometric process for the estimation of reducing sugars has been examined by a number of investigators, the chief of these being Rouijn (*Z. anal. Chem.*, 1897, **36**, 349), Bougault (*Compt. rend.*, 1917, **164**, 1008), Willstätter and Schudel (*Ber.*, 1918, **51**, 780), Judd (*Biochem. J.*, 1920, **14**, 255), Baker and Hulton (*Biochem. J.*, 1920, **14**, 754), Cajori (*J. Biol. Chem.*, 1922, **64**, 617), Kolthoff (*Z. Untersuch. nehr. Genussm.*, 1923, **45**, 131, 141), Hinton and Macara (*Analyst*, 1924, **49**, 2), and Gobel (*J. Biol. Chem.*, 1927, **72**, 801). They investigated the oxidation of glucose by iodine in the presence of either borax, sodium carbonate, or caustic soda for particular purposes. Allen and Winegarden (*J. Biol. Chem.*, 1923, **88**, 225) studied the rate of oxidation of glucose by iodine in presence of insulin. Kappanna (*J. Indian Chem. Soc.*, 1928, **5**, 387) studied the effect of phosphates and p_H on the reaction between dextrose and iodine.

The effect of the following neutral salts, viz., chlorides, bromides and nitrates of sodium, ammonium and potassium and potassium iodide has been studied on this reaction.

EXPERIMENTAL.

$N/10$ -Iodine solution (50 c.c.), $M/20$ -glucose solution (50 c.c.), $N/20$ -NaOH solution (20 c.c.), required amount of the neutral salt solution and distilled water to keep the volume constant, were taken together in a stoppered bottle using a thermostat at 30° . After allowing the mixture to stand for 40 minutes, 10 c.c. of this reaction mixture were taken out in a conical flask containing 25 c.c. of about $N/80$ - $Na_2S_2O_3$ solution. The solution was then acidified with 5 c.c. of semi-normal H_2SO_4 and the excess of thio-sulphate was immediately titrated back against about $N/400$ -iodine solution with starch as indicator. In this way a number of readings were taken using three concentrations of the neutral salts.

TABLE I.
Temp. = 30° .

Salt soln. added.	K salts ($\times 10^5$).			Na salts ($\times 10^5$).			Ammon. salts ($\times 10^5$).		
	KCl	KBr.	KNO_3 .	NaCl.	NaBr.	$NaNO_3$.	NH_4Cl .	NH_4Br .	NH_4NO_3 .
50 c.c.	4.638	4.638	4.638	4.638	4.638	4.638	4.638	4.638	4.638
5	4.380	4.420	4.420	4.200	4.210	4.330	3.930	4.160	4.350
10	3.875	4.056	4.270	3.860	3.900	4.100	3.530	3.530	3.866
20	3.341	3.630	3.860	3.124	3.467	3.730	2.857	3.215	3.630

DISCUSSION.

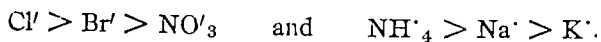
From Table I, it is concluded that by adding neutral salts, *viz.*, chlorides, bromides and nitrates of potassium, sodium and ammonium, the speed of the oxidation of glucose by iodine is retarded, and the velocity constant of the reaction decreases with increasing concentration of the salts. The variation in the velocity constant with these different salts show that the value of K for a given concentration of the salt is not independent of the nature of the added salt.

The comparative results of all salts are summarised in the following table.

TABLE II.

Salts.	Salt soln. added at $30^{\circ}=20$ c.c.		
	Chloride	Bromide.	Nitrate.
Potassium	3.341×10^{-5}	3.630×10^{-5}	3.860×10^{-6}
Sodium	3.124	3.467	3.730
Ammonium	2.857	3.215	3.630

Table II shows that the oxidation of glucose by sodium hypoiodite is retarded in the order given below.



The decrease in the velocity constant can be attributed to the formation of complex ions between iodine and halide ions. This may be due to the fact that there the number of free ions becomes less, and complex iodine ions as in the case of potassium iodide ($\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$) predominate. Where no such formation of complex takes place as in the case of nitrates, the velocity constant is hardly affected. The case of ammonium nitrate is an exception which shows that iodine forms some complex ions with ammonia as is well known, and also when ammonium salts are added the diminution in velocity may be due to diminution of p_{H} due to reaction between NH_4' and OH' of NaOH . Thus it may be assumed that the free iodine ions are active in the reaction.

A NOTE ON AN ISOMER OF DIMETHYLETHYL-PYRIDINE.

BY RAFAT HUSAIN SIDDIQUI.

The author was busy with a new synthesis of 2-methyl-4-ethylpyridine in order to identify some of the products of alkaline degradation of strychnine and brucine (*J. Indian Chem. Soc.*, 1939, **16**, 396, 399) and in this connexion he prepared potassium salt of 2:6-dimethyl-4-ethylpyridine -3:5-dicarboxylic acid which gave normally 2:6-dimethyl-4-ethylpyridine but in one case the potassium salt was not decarboxylated for long and the product after mixing with soda lime was left in a beaker for four months (May to August during summer and rainy season) Afterwards, it was found that it had absorbed sufficient moisture and turned pasty. After drying at 100° in an air-oven it was distilled and it did not give even a trace of 2:6-dimethyl-4-ethylpyridine but a mixture of bases (a) b.p. 193-196°, (b) b.p. 217°-220°. The latter was not sufficient for further characterisation but the former was converted into its picrate. The picrate was decomposed with aqueous sodium hydroxide and the base, extracted with petroleum ether, was washed with water and dried over anhydrous potassium carbonate. On removal of the solvent the base distilled completely at 195-96° and was soluble in common organic solvents. It had strong smell of pyridine and like 2:6-dimethyl-4-ethylpyridine it did not fume in air. Owing to its volatility it could not be dried at 100° in *vacuo* and an undried sample of the material appeared to retain 1/4 mol. of water. (Found in an undried sample: C, 76.83; H, 9.26; N, 9.88, $C_8H_{13}N$, 1 1/4 H_2O requires C, 76.75; H, 9.52; N, 9.76 per cent). The base gave crystalline salts with definite melting points.

The *hydrochloride* was prepared as a snow white crystalline mass from a solution of the base in ether by the addition of ethereal hydrogen chloride and recrystallised from alcohol in perfectly white thick prisms, m. p. 197°, and remained as such even after one year (2:6-dimethyl-4-ethylpyridine hydrochloride, prepared likewise, was hygroscopic, pinkish long needles, m. p. 97°, and on keeping turned liquid). It was soluble in alcohol, acetone, chloroform and water. (Found in material dried at 100° in *vacuo*: C, 62.95; H, 8.07; N, 8.72; Cl, 21.11. $C_8H_{13}N$, HCl requires C, 62.97; H, 8.16; N, 8.16; Cl, 20.7 per cent). The *hydriodide* was prepared by mixing together alcoholic solutions of the hydrochloride and potassium iodide. The solution after addition of a little water was filtered and the residue on removal of the solvent was dissolved in ethyl acetate when the hydriodide separated in needles at room temperature. It is soluble in water, benzene, chloroform, and alcohol, m. p. 155°.

The *Ethiodide* in poor yield was obtained by mixing together chloroform solution of the base (1 mol.) and ethyl iodide (1.5 mol.) at room temperature as needles, m. p. 185°. It is soluble in alcohol, acetone, benzene, chloroform and water.

The *Platinichloride* came down from dilute alcohol at 0° in golden yellow needles. It is soluble in chloroform, m.p. 222° (platinichloride of 2:6-dimethyl-4-ethylpyridine, m.p. 210°-211°; mixed m.p. 179°-181°). At 100° it lost 5.7% (H₂O requires 2.6 per cent). [Found in material dried at 100° in *vacuo*: C, 32.01; H, 4.22; N, 3.83; Pt, 28.58. (C₈H₁₃N, HCl)₂.PtCl₄ requires C, 31.77; H, 4.20; N, 4.12; Pt, 28.70 per cent].

The *Aurichloride* was prepared from dilute alcohol and was recrystallised from ethanol with a drop of gold chloride in yellow needles. It is soluble in alcohol; ethyl acetate, acetone, benzene and chloroform, m.p. 180°.

The *Picrate* was prepared by bringing together the solution of the base and picric acid and crystallised from hot methanol in lemon-yellow needles, m. p. 167° (2:6-dimethyl-4-ethylpyridine picrate, m. p. 120° and mixed m. p. 110°-135°). It lost at 100° in *vacuo* half a molecule of water of crystallisation (Found: H₂O, 2.3; $\frac{1}{2}$ H₂O requires 2.4 per cent). [Found in material dried at 100° in *vacuo*: C, 49.64; H, 4.53; N, 15.59. C₈H₁₃N · C₆H₃(NO₂)₃(OH) requires C, 49.50; H, 4.40; N, 15.4 per cent].

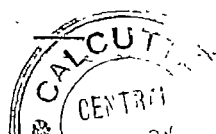
From the analyses and other experimental observations it is quite evident that the base (a) b p. 195-96° agrees with formula C₈H₁₃N and is not identical with 2:6-dimethyl-4-ethylpyridine and other known bases of the series as the following comparison would show. The quantity was not sufficient for further work.

C ₈ H ₁₃ N	Hydrochloride.	Picrate	Platini chloride.	Auri. chloride.
2:6-Dimethyl-4-ethylpyridine, b. p. 186° (<i>Annalen</i> , 281, 44; <i>J. Indian Chem. Soc.</i> , 1939, 16, 410, 415)	97°	120°	210°-211°	„
2-Ethyl-3:5-dimethylpyridine, b. p. 197°-199° (<i>Ber.</i> , 1890, 23, 685, 1110; <i>J. Russ. Phys. Chem. Soc.</i> , 1923, 64, 428)	„	„	189°	81°-82° 86°-87°
2:5-Dimethyl-6-ethylpyridine, b. p. 181°-182° (<i>J. Indian Chem. Soc.</i> , 1935, 12, 665).	„	127°	„	„
2:6-Dimethyl-3-ethyl pyridine, b. p. 83-85°/23mm (<i>Ber.</i> , 1925, 68B, 194)	„	162°	178°	„
2:3:4:6-Tetramethyl pyridine, b. p. 180°-195° (<i>Ber.</i> , 1931, 64B, 569)		168°-70°	„	„
Base (a) b. p. 195°-196°	197°	167°	220°	180°

The micro-analyses were done by Dr. Ing. A. Schöller, Berlin.

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Received May 17, 1941.





STUDIES ON THE PHOTOCHEMICAL ACTIVITY OF MIXTURES OF VANADIC ACID AND TARTARIC ACID.

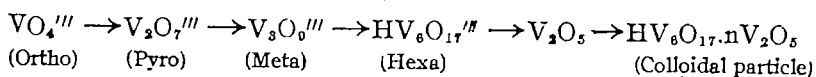
PART I. OPTICAL PROPERTIES OF MIXTURES OF VANADIC ACID AND TARTARIC ACID.

REDUCTION OF THESE MIXTURES IN LIGHT AND IN THE DARK.

By T. L. RAMA CHAR.

The relationship between the hydrogen ion concentration and (i) optical rotation, (ii) light absorption and (iii) dark reaction of mixtures of vanadic and tartaric acids has been investigated. The reduction of vanadic acid by racemic-tartaric acid in the dark has been found to give a higher value for the velocity of the reaction than that for the reduction by *d*-, or *l*-, or *dl*-tartaric acids, at the same hydrogen ion concentration. The photoreduction of mixtures of vanadic acid and tartaric acid has been studied in the visible and ultraviolet regions.

Biltz (*Ber.*, 1904, **37**, 1098) found that the reddish brown product obtained by the addition of dilute hydrochloric acid to ammonium metavanadate gives a reddish yellow colloidal solution of vanadium pentoxide on being washed with distilled water. Dumansky (*Kolloid Z.*, 1923, **33**, 147), found that the red sol of vanadic acid contains negatively charged particles, and postulated that by the addition of hydrochloric acid to salts of orthovanadic acid, the following changes occur :



i.e. with progressive increase in the number of atoms of vanadium in a molecule of vanadic acid, the colloid chemical properties become more and more manifest. Dumansky (*loc. cit.*) has also shown that the pentoxide sols on being treated with reducing agents furnish the sols of lower oxides of vanadium which are also negatively charged.

Vanadic acid sol displays peculiar optical phenomena. Freundlich *et al* (*Koll.-chem. Beih.*, 1915, **7**, 195 ; *Z. physikal. Chem.*, 1924, **114**, 161) have studied the phenomena of streaming double refraction and dichroism in vanadic acid sol. Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 189) showed that a freshly prepared colloidal solution is not birefringent; on keeping it slowly develops double refraction due to the formation of needle-shaped micro-crystalline micelles. Kruyt (*Kolloid Z.*, 1916, **19**, 16) concluded that the orientation was due to the cataphoretic motion of rod-shaped particles. Marshall (*Trans. Faraday Soc.*, 1930, **26**, 173) has

studied the electrical double refraction of a 6-year old sol and has shown that the orientation of anisotropic particles depends primarily on their fundamental electrical properties. Lange (*Z. physikal. Chem.*, 1928, **132**, 21) studied the polarisation of the Tyndall light from the sol and concluded that the particles were not spherical in shape. Zocher and Jacobsohn (*Kolloid Z.*, 1927, **41**, 220) showed that some sols of vanadium pentoxide spontaneously separate into two phases—one is isotropic and dilute, the other anisotropic and concentrated.

Vanadic acid becomes markedly photo-sensitive when exposed to light with organic substances like tartaric acid, glycerol, benzaldehyde, etc. It blackens and undergoes reduction, giving rise initially to the tetroxide (Gibbons, *Chem. News*, 1874, **30**, 267, 1874; Renz, *Helv. Chim. Acta*, 1921, **4**, 961).

In the present investigation, the optical and photochemical properties of vanadium compounds have been studied in the p_H range 1.4 to 6.6 where vanadic acid exists either as polyvanadic acid sol or as vanadate.

A. Optical Properties of Mixtures of Vanadic Acid and Optically Active Tartaric Acid at low p_H .

(a) *Optical Rotation*.—When *d*- or *l*-tartaric acid is added to sodium metavanadate ($\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$), the mixture has an optical rotation which is *opposite* in sign to the rotation of the tartaric acid used. It was found that an addition of hydrochloric acid to this mixture, i.e., increase in $[\text{H}^+]$, the rotation gradually decreased. The relationship between the rotation and the $[\text{H}^+]$ of the mixture was studied by using equimolecular mixtures of vanadic and tartaric acids at p_H 4, and increasing the $[\text{H}^+]$ by addition of hydrochloric or tartaric acids, keeping the final concentration of the mixture the same in each case.

The changes in the rotation of the mixture were followed in yellow light with a Winkel-Zeiss triple-field polarimeter which gave readings to $\pm 0.01^\circ$. The measurements were made in the shortest possible time in order to avoid the error that is likely to be introduced due to the dark reaction at very low p_H . The chemicals used were all either Merck's or Kahlbaum's samples, and tartaric acids were recrystallised before use. 'conductivity water' was used throughout for preparing the solutions. The p_H of the mixtures was measured by means of the glass electrode. The results obtained by adding hydrochloric acid to an equimolar mixture of vanadic acid and *d*-tartaric acid are given below. The concentration of vanadate is always given as amount of pentavalent vanadium,

TABLE I.

Length of solution (d) = 2.5 cm. $\lambda = 5893\text{\AA}$. Temp. = 25°.

Conc. of vanadium in starting mixture.

0.033 M Rotation of Mixture. Free H_2T .*		0.025 M Rotation of Mixture. Free H_2T .*		0.017 M Rotation of Mixture. Free H_2T .*	
$[\text{H}^+]$		$[\text{H}^+]$		$[\text{H}^+]$	
1×10^{-4}	-0.18° < +0.02°	1×10^{-4}	-0.12° < +0.02°	1×10^{-4}	-0.08° < +0.01°
25	-0.13	13	-0.10	37	-0.05
50	-0.10	89	-0.05	100	-0.03
76	-0.08	190	-0.03		
130	-0.06				

* H_2T = Tartaric acid.

The results show that the rotation of the mixture is negative and it decreases with increase in $[\text{H}^+]$. Columns 3, 6 and 9 of the above table give the rotation that should have been observed if all the d -tartaric acid were present alone as free molecules in solution. It shows that the magnitude of mixture is much higher than that of free tartaric acid. Some rotation measurements were made by varying the $[\text{H}^+]$ by an increase in the concentration of d -tartaric acid. The results are given below :

TABLE II.

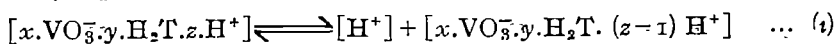
Other conditions same as in Table I.

Conc. of d -tartaric acid.	Conc. of vanadium.	$[\text{H}^+]$.	Rotation of Mixture.	Rotation of Free H_2T .
0.025 M	0.025 M	1×10^{-4}	-0.12°	< +0.02°
0.033	"	13	-0.10	< +0.02
0.067	"	89	-0.05	< +0.03
0.100	"	190	-0.03	< +0.05

The results show that if d -tartaric acid itself is used to increase the $[\text{H}^+]$ in place of hydrochloric acid, the observed rotations are identical for the same p_n , with those given in Table I. Table II, column 5 gives the calculated value of the rotations if the whole of d -tartaric acid existed in solution as free molecules.

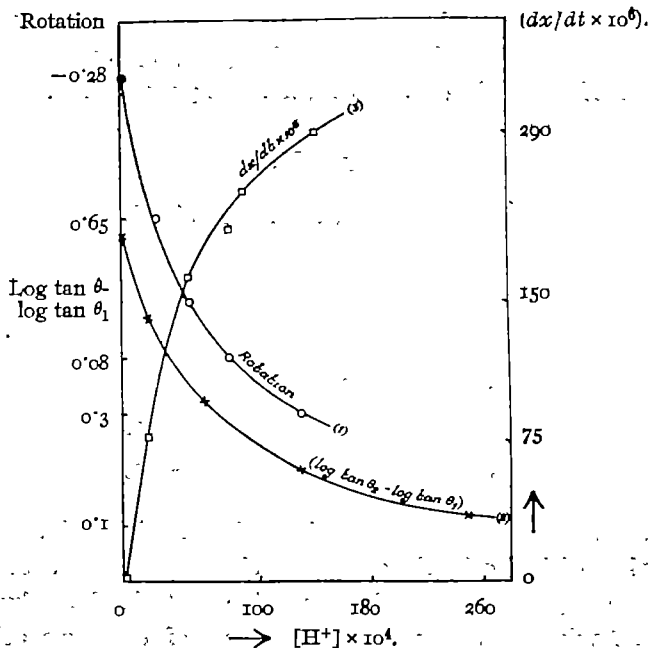
It is clear that the solution does not contain any free tartaric acid even when the ratio $\text{H}_2\text{T} : \text{NaVO}_3 = 4 : 1$, but negatively charged poly-vanadic

acid-tartaric acid micelles having the composition $[x.VO_3^-, y.H_2T, z.H^+]$, where x/y is as the ratio of the molar concentrations of vanadate and tartaric acid respectively. These micelles have a negative optical rotation even though *d*-tartaric acid enters into the formation of the colloidal micelle. Again, the magnitude of the rotation is independent of the ratio of x/y , but is dependent on the p_H of the environment and the vanadate content of the solution as will be clear from Table I. We have, therefore, to postulate an ionic adsorption equilibrium of the type



If it is assumed that the micelle with the larger negative charge $[x.VO_3^-.y.H_2T.(z-1)H^+]$ has a negative rotation very much greater than that of the micelle $[x.VO_3^-.y.H_2T.H^+]$ and that the concentration of the former is inversely proportional to the $[H^+]$, the experimental results can be explained almost quantitatively. Fig. 1 (curve 1) shows that the optical rotation of the colloidal micelle is approximately in inverse proportion to the $[H^+]$, indicating that the concentration of the micelle $[x.VO_3^-.y.H_2T.(z-1)H^+]$ is approximately in inverse proportion to the $[H^+]$.

FIG. 1.



Light Absorption.

When tartaric acid (*d*-, *l*- or *r*-) is added to sodium metavanadate, a deep red colour is developed: the mixture has a high extinction coefficient

in blue light. Addition of hydrochloric acid to this mixture resulted in the colour gradually fading to orange, yellow and finally pale yellow, and the light absorption of the mixture decreased. This decrease in light absorption runs parallel with the decrease in rotation. The relationship between the absorption and the $[H^+]$ was studied according to the method described for rotation measurements. The absorption was measured by the König-Marten spectrophotometer which was calibrated for 4916\AA , the wavelength in which the readings were taken. The results obtained by increasing the $[H^+]$ of equimolar mixtures of *d*-tartaric acid and vanadate at p_H 4 by the addition of hydrochloric acid, are given below.

TABLE III.

Length of solution (*d*) = 0.5 cm. $\lambda = 4916\text{\AA}$. Temp. = 25° .

0.033 M.		Conc. of starting mixture. 0.025 M.		0.017 M.	
$[H^+]$	$\epsilon, c, d.$ *	$[H^+]$	$\epsilon, c, d.$	$[H^+]$	$\epsilon, c, d.$
1×10^{-4}	0.62	1×10^{-4}	0.47	1×10^{-4}	0.29
20	0.47	21	0.36	20	0.22
63	0.32	91	0.19	100	0.11
130	0.20	210	0.11	280	0.05
250	0.12	350	0.07		

* ϵ = Extinction coeff. C = Conc.

The absorption decreases with increase in $[H^+]$ of the mixture. The value of the extinction coefficient, like the optical rotation, simply depends on the p_H and the vanadate content of the solution. Table IV shows that similar results are obtained if *d*-tartaric acid is used to increase the $[H^+]$ in place of hydrochloric acid.

TABLE IV.

Other conditions same as in Table III.

Conc. of <i>d</i> -H ₂ T.	Conc. of vanadium ₅	$[H^+]$	$\epsilon, c, d.$
0.033 M	0.033 M	1×10^{-4}	0.62
0.050	"	20	0.47
0.083	"	79	0.28
0.125	"	140	0.19
0.167	"	360	0.09

The experimental observations on the extinction coefficients of polyvanadic acid-tartaric acid micelles lend support to the assumptions made in explaining the observed optical rotations of such micelles. In the adsorption

equilibrium equation (i) the more negatively charged micelle $[x.VO_3^- \cdot y.H_2T \cdot (z-1)H^+]$ is red-orange in colour and has a high extinction coefficient in blue light. As the $[H^+]$ is increased, the colour fades from yellow to pale yellow, the extinction coefficient decreases and we have the less negatively charged micelle $[x.VO_3^- \cdot y.H_2T \cdot z.H^+]$. Fig. 1 (curve 2) shows that like the optical rotation, the light absorption of the colloidal micelle is approximately in inverse proportion to $[H^+]$; this indicates that the concentration of the micelle $[x.VO_3^- \cdot y.H_2T \cdot (z-1)H^+]$ is approximately in inverse proportion to the $[H^+]$.

Experiments with d-, l-, and r-Acids.

Some experiments on the optical rotation and light absorption of vanadic acid-tartaric acid mixtures were carried out with *l*- and racemic tartaric acids. The results showed that mixtures of *d*- and *l*-acids with vanadic acid give rotations which are equal in magnitude but opposite in sign, at the same $[H^+]$. Again, a mixture containing *d*- or *l*-acid has a rotation which is opposite in sign to the rotation of the free tartaric acid. A mixture of racemic acid and vanadic acid has no rotation.

In absorption measurements, no difference was obtained for the absorption of mixtures containing *d*-, *l*-, or *r*-acids, at the same $[H^+]$.

B. Reduction of Mixtures of Vanadic Acid and Tartaric Acid in the Dark at low p_H .

Detailed investigation of the effect of p_H on the reduction of penta-valent vanadium by tartaric acid (from polyvanadic acid sol to polyvanadous acid sol) in the dark showed that, for all mixtures of tartaric acid and sodium vanadate, there is a definite $p_H = 4$, above which there is no dark reaction; below this p_H , the dark reaction proceeds, its velocity increasing with decreasing p_H i.e., increasing $[H^+]$ of the mixture. It was shown in Sec. A that an increase in the $[H^+]$ of vanadic acid-tartaric acid mixtures results in a decrease in the optical rotation and light absorption. These changes are simultaneously accompanied by an increase in the velocity of the dark reaction.

The reaction was followed by estimating the vanadium according to the method of Furman (*Ind. Eng. Chem.*, 1925, 17, 314). The mixture to be estimated was titrated in sulphuric acid solution (final acid concentration being 30 c.c. acid of sp. gr. 1.84 in 1 litre) with ferrous sulphate using a freshly prepared 0.1% sulphuric acid solution of diphenylamine as indicator.

The effect of variation of the $[H^+]$ on the velocity of the reaction was studied by varying the concentration of *d*-tartaric acid, keeping the

initial concentration of vanadate (as pentavalent vanadium) constant. Table V below gives the observed values of the velocity. The value of dx/dt is given as the number of g. mols transformed per minute at the beginning of the reaction.

TABLE V.

Temp. = 25°.

Conc. of $d\text{-H}_2\text{T}$. Vanadium.		$[\text{H}^+]$.	$\frac{dx}{dt}$.	Conc. of $d\text{-H}_2\text{T}$. Vanadium.		$[\text{H}^+]$.	$\frac{dx}{dt}$.
0.033 M	0.033 M	1×10^{-4}	—	0.063	0.025	57×10^{-4}	122×10^{-6}
0.050	„	20	78×10^{-2}	0.083	„	120	160
0.067	„	50	162	0.100	„	190	187
0.083	„	79	189	0.125	„	220	200
0.100	„	89	205	0.017	0.017	1	—
0.125	„	140	240	0.025	„	9	20
0.167	„	360	290	0.033	„	33	55
0.025	0.025	1	—	0.050	„	60	81
0.031	„	7	24	0.056	„	79	94
0.050	„	28	75	0.083	„	180	125

The velocity of the reaction increases with increase in $[\text{H}^+]$. The effect of variation of $[\text{H}^+]$ on the velocity was also studied by the addition of hydrochloric acid to an equimolar mixture of vanadic acid and tartaric acid. The results are given below.

TABLE VI.

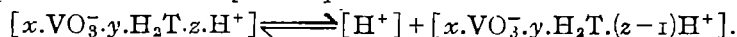
Temp. = 25°.

Concentration of vanadium in starting mixture

0.050 M		0.033 M		0.025 M		0.017 M	
$[\text{H}^+]$.	dx/dt .	$[\text{H}^+]$.	dx/dt	$[\text{H}^+]$	dx/dt .	$[\text{H}^+]$.	dx/dt .
1×10^{-4}	—	1×10^{-4}	—	1×10^{-4}	—	1×10^{-4}	—
3	19×10^{-6}	14	62×10^{-6}	14	46×10^{-6}	14×10^{-6}	31
14	92	50	162	50	122	50	81
50	243	79	189	200	187	200	125
200	375	200	250				

Tables V and VI clearly show that it does not matter whether *d*-tartaric acid or hydrochloric acid is used to increase the $[H^+]$; the result is the same. The velocity of the dark reaction, like the optical rotation and light absorption, depends only upon the p_H and the vanadium content of the solution. In fact, the value of dx/dt , at the same p_H , is directly proportional to the concentration of vanadium (Table VI).

It appears that the hypothesis of ionic adsorption equilibrium for polyvanadic acid-tartaric acid micelles, which could reasonably explain the optical properties of such micelles, can also explain the experimental results on the dark reaction. Colloidal micelles of the type $[x.VO_3^- \cdot y.H_2T \cdot z.H^+]$ exist in equilibrium with the hydrogen ions in the solution, and the equation for the adsorption equilibrium is



The more negatively charged micelle $[x.VO_3^- \cdot y.H_2T \cdot (z-1)H^+]$ does not undergo reduction in the dark at p_H equal to and greater than 4. As the $[H^+]$ is increased, the velocity of the dark reaction gradually increases and we have the micelle $[x.VO_3^- \cdot y.H_2T \cdot z.H^+]$, which is responsible for the reduction in the dark. Fig. 1 (curve 3) in Sec. A shows that, whereas the optical rotation and light absorption are approximately in inverse proportion to the $[H^+]$, the velocity of the dark reaction is approximately proportional to the $[H^+]$. This means that the concentration of the micelle $[x.VO_3^- \cdot y.H_2T \cdot z.H^+]$ is approximately proportional to the $[H^+]$.

Dark Reaction with d-, l-, dl- and r-Acids.

It is usually held that racemic compounds only exist in the crystalline condition and that when they are dissolved they dissociate into simple mixtures of two externally compensated optical isomers, (Jaeger, "Le Principe de Symetric et ses applications," Paris, p. 245). On the other hand, Cotton (*Trans. Faraday Soc.*, 1930, **26**, 377) has pointed out to the distinction that must be made between the solution of a racemate and simple mixture which is inactive by external compensation. From his observations on the differences in light absorption of alkaline solutions of copper racemate and *d*- or *l*-tartrate, Cotton (*Ann. chim. phys.*, 1896, **8**, 347) concludes that there are some racemic compounds which can be dissolved without complete dissociation. Similar results have been obtained by Gabiano (*Compt. rend.*, 1927, **184**, 1059) and De Malleman and Gabiano (*ibid.*, 1927, **188**, 350) with copper racemate and tartrate solutions.

In the present investigation, the reduction of a mixture of vanadic acid and racemic-tartaric acid in the dark gave a higher value, at the same

p_H , for the velocity than that for *d*-tartaric acid, whereas the *l*-acid as well as the *dl*-mixture (mixture of *d*- and *l*-acids in equimolar proportions) gave the same velocity as *d*-acid. The results obtained are given below.

TABLE VII.

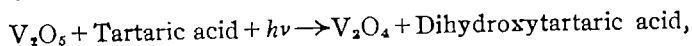
Temp. = 25°.

Concentration of H ₃ T. Vanadium.		[H ⁺].	$\frac{dx}{dt} \times 10^6$.			
			<i>d</i> -H ₃ T	<i>r</i> -H ₃ T	<i>l</i> -H ₃ T	<i>dl</i> -H ₃ T.
0.167 <i>M</i>	0.033 <i>M</i>	360×10^{-4}	290	370	290	290
0.125	"	140	240	304		
0.100	"	89	205	270		
0.083	"	79	189	239		
0.050	"	20	78	103	80	78
0.125	0.025	220	200	255	200	202
0.100	"	190	187	237		
0.083	"	120	160	199		
0.063	"	57	122	160		
0.050	"	28	75	104	75	75
0.031	"	7	24	34		
0.083	0.017	180	125	161	122	125
0.056	"	79	94	132		
0.050	"	60	81	100	81	81
0.033	"	33	55	80		
0.025	"	9	20	30		

The differences in velocity that are obtained with racemic-acid are very large (between 25 to 50%). It appears peculiar that the racemic-acid mixture should give a higher value for the velocity whereas the *dl*-mixture gives the same value as that for *d*- or *l*-acid. It is probable that the colloidal micelle of racemic-acid and vanadic acid is different from that of the micelle containing *d*- or *l*- or *dl*-acids.

C. Photoreduction of Mixtures of Sodium Vanadate and Tartaric Acid at p_H greater than 4.

A mixture of vanadic acid and tartaric acid is photosensitive to ultraviolet as well as to visible light, and undergoes photoreduction :



the colour change being from red or yellow to greenish-black, blue or violet, depending upon the p_H . At low p_H , the dark reaction is rapid, and the photochemical reaction is small. As the p_H is increased, the light reaction

becomes more appreciable, and at p_H , 4 the dark reaction disappears and only the photoreaction proceeds.

The kinetics of the photoreduction has been studied in the ultraviolet, blue and green regions. The vanadium content (in the pentavalent state) of the mixture was estimated as before.

EXPERIMENTAL.

The source of light was a quartz-mercury arc lamp which was run from a battery of 220 volts, at a constant current of 1.6 amperes. Light from the lamp was rendered parallel by means of quartz cylindrical lenses and passed into the reaction vessel kept inside a double-jacketed box, which was maintained at constant temperature by circulating water from a thermostat through its annular space. The reaction vessel was a rectangular stoppered cell (1.8 cm. \times 1.8 cm. \times 0.5 cm.) made of plane parallel plates of fused transparent quartz, the joints being fused to one another. The following filters were used to isolate the required monochromatic radiations:

3130Å	...	Ultraviolet filter, (Chance Bros.)
4360Å	...	Zeiss monochromatic filter
5460Å	...	" " "

In addition, water or 1% CuSO_4 filters were used to cut off the infra-red radiation.

The intensity of the incident radiation was varied by using lenses of different focal lengths. The thickness of the cell was on purpose made as small as possible so that the liquid inside may be considered to have a practically homogeneous light intensity in different layers. The intensity of the absorbed radiation was measured by means of a Moll thermopile and Moll galvanometer. The thermopile was frequently calibrated by means of a standard lamp supplied by the Bureau of Standards. The absorbed intensity was determined by observing the galvanometer deflections with water and then with the reaction mixture in the cell. During the measurements, the thermopile was always placed at the same position, immediately behind the reaction cell.

Above p_H 4 tartaric acid is mostly dissociated into HT^- ion, and equimolecular complex ions of the type $[\text{VO}_3.\text{HT}^-]$ appear to exist in solution. Even in the p_H region 4.3 to 6.6, the vanadate-*d*-tartaric acid mixture has a negative optical rotation, the value being as high as -0.18° at p_H 5.3. The photoreduction of such mixtures was studied, with the concentration of vanadate greater than that of tartaric acid in all cases, i.e. concentration of equimolar complex ion is equal to concentration of

tartaric acid. It is clear that there is no free tartaric acid in solution, but only free vanadate ions in all these mixtures.

The reaction was studied in the visible as well as in the ultraviolet. It is zero molecular with respect to vanadate (pentavalent vanadium) and there is no dark reaction. Table VIII gives the effect of varying the concentration of the reactants on the velocity of the photoreduction. *d*-Tartaric acid has been used and dx/dt refers to the number of g. mols transformed per minute.

Reaction in the Ultraviolet.

TABLE VIII.

Effect of varying the concentration.

$\lambda = 3130 \text{ \AA}$, Temp. = 28° . $p_H = 4.3$ to 5.7 . $I_{abs.} = 10294$ ergs for all the mixtures.

		$(dx/dt) = I_{abs.} \times 5.38 \times 10^{-7} \times \frac{\text{Conc. of equimol. complex ion.}}{1 + (18.5 \times \text{conc. of free vanadate ion})}$	
Concentration of H_2T .	$NaVO_3$.	$dx/dt \times 10^5$	
		Obs.	Calc.
0.050 M	0.100 M	14.1	14.4
0.025	0.050	9.2	9.5
0.017	0.033	7.1	7.1
0.013	0.025	5.9	5.6
0.008	0.017	4.3	4.0
0.017	0.025	8.0	8.0
0.013	"	5.9	5.6
0.008	"	3.6	3.5
0.006	"	2.5	2.6
0.004	"	1.8	1.7
0.025 M	0.33 M	10.8	12.0
0.017	"	7.1	7.1
0.013	"	5.3	5.0
0.010	"	4.0	3.9
0.008	"	3.3	3.2
0.006	"	2.4	2.3
0.013	0.017	6.5	6.4
0.010	"	5.0	4.9
0.008	"	4.3	4.0
0.006	"	3.2	3.0
0.004	"	1.9	1.9

The velocity of the reaction decreases with decrease in equimolar concentration.

The effect of varying the intensity of the absorbed radiation of the velocity of the reaction is given below.

TABLE IX.

Effect of varying the intensity of the absorbed radiation.

$\lambda = 3130 \text{ \AA}$. Temp. = 28° . $p_H = 5.2$.

Conc. of H_2T	Conc. of $NaVO_3$	$I_{abs.}$	dx/dt .
0.050 M	0.100 M	10294 ergs.	14.1×10^{-5}
"	"	4428	6.3
"	"	1125	1.6
0.025	0.050	10294	9.2
"	"	4498	4.0

For the same mixture, the value of dx/dt is proportional to $I_{abs.}$

Reaction in the Blue.

TABLE X.

Effect of varying the concentration. $\lambda = 4360 \text{ \AA}$ $I_{\text{abs.}} = 7440$ ergs for all mixtures. Temp. = 28° . $p_H = 5.3$ to 6.6 . $dx/dt =$ same as in Table VIII.

Concentration of $\text{H}_2\text{T.}$ NaVO_3		$dx/dt \times 10^5$ Obs Calc		Concentration of $\text{H}_2\text{T.}$ NaVO_3		$dx/dt \times 10^5$ Obs. Calc.	
0.125 M	0.250 M	15.3	15.1	0.125 M	0.250 M	15.3	15.1
0.083	0.167	12.8	13.0	0.083	"	8.5	8.2
0.050	0.100	10.2	10.3	0.063	"	6.1	5.7
0.025	0.050	7.0	7.0	0.050	"	4.8	4.3
0.017	0.033	5.5	5.6	0.025	"	2.2	2.0
0.013	0.025	4.2	4.1				
0.050	0.100	10.2	10.3	0.025	0.050	7.0	7.0
0.033	"	5.7	5.9	0.017	"	4.5	4.1
0.025	"	4.2	4.2	0.013	"	3.2	3.0
0.017	"	2.8	2.6	0.008	"	2.3	2.0
0.013	"	2.1	2.0	0.006	"	1.5	1.4

The above results are of the same type as those obtained for the reaction in the ultraviolet, the velocity of the reaction decreasing with decreasing equimolar concentration. Table XI shows that the velocity of the reaction in blue light is proportional to the intensity of the light absorbed.

TABLE XI.

Effect of varying the absorbed intensity. $\lambda = 4360 \text{ \AA}$. Temp. = 28° . $p_H = 5.2$

Conc. of $\text{H}_2\text{T.}$	Conc. of NaVO_3	$I_{\text{abs.}}$	dx/dt .
0.125 M	0.250 M	7440 erg.	15.3×10^{-5}
"	"	5017	10.0
"	"	3720	7.7
0.050	0.100	7440	10.2
"	"	3720	5.1

Reaction in the Green.

The photoreduction in the green region gave the following results.

TABLE XII.

Effect of varying the concentration.

$\lambda = 5460 \text{ \AA}$. Temp. = 28° . $p_H = 5.4$ to 6.6 .

$$(dx/dt) = I_{\text{abs}} \times 2.89 \times 10^{-7} \times \frac{\text{conc. of equimol. complex ion.}}{1 + (18.5 \times \text{conc. of free vanadate ion})}$$

Conc. of H_2T .	Conc. of NaVO_3 .	I_{abs} .	$dx/dt \times 10^6$.	
			obs.	calc.
0.125 M	0.250 M	7698 ergs.	8.5	8.4
0.083	0.167	7577	7.2	7.2
0.050	0.100	7440	5.6	5.6
0.025	0.050	6747	3.2	3.3
0.017	0.033	5882	2.2	2.2
0.125	0.250	7698	8.5	8.4
0.083	"	"	4.4	4.5
0.050	"	"	2.5	2.4
0.031	"	"	1.4	1.4
0.025	"	"	1.1	1.1
0.083	0.167	7577	7.2	7.2
0.056	"	"	3.6	3.8
0.042	"	"	2.7	2.7
0.028	"	"	1.6	1.7
0.021	"	"	1.3	1.3

TABLE XIII.

Effect of varying the absorbed intensity.

$\lambda = 5460 \text{ \AA}$. Temp. = 28° . $p_H = 5.2$.

Conc. of H_2T .	Conc. of NaVO_3 .	I_{abs} .	dx/dt
0.125 M	0.250 M	7698 ergs.	7.5×10^{-4}
"	"	5363	5.0
"	"	3892	3.7
0.083	0.167	7577	6.0
"	"	5363	4.2

Table XII shows that the value of dx/dt decreases with decrease in equimolar concentration. Table XIII shows that the velocity is proportional to I_{abs} .

Reaction with d-, l- and r-Acids.

Some experiments were carried out wherein *l*- and *r*-tartaric acids were the photo-active reductants. The results given in Table XIV below show that there is no difference in the velocity of the photoreduction with these acids in all the wave-lengths studied. The dark reaction, on the other hand, gave a higher value for the velocity with racemic acid as reductant.

TABLE XIV.

$p_H = 5.2$. Temp. = 21° . I_{abs} is the same for mixtures of *d*-³⁶*l*- or racemic-acids.

Wave-length (λ).	Concentration of		I_{abs} .	$dx/dt \times 10^6$.		
	H_2T .	$NaVO_3$.		<i>d</i> - H_2T .	<i>l</i> - H_2T .	<i>r</i> - H_2T .
3130Å	0.050 M	0.100 M	10294 ergs	14.1	14.1	14.3
"	0.025	0.050	"	9.2	9.1	9.2
"	0.017	0.033	"	7.1	7.1	7.2
4360	0.050	0.100	7440	10.2	10.2	10.3
"	0.025	0.050	"	7.0	7.0	7.0
5460	0.050	0.100	"	5.6	5.7	5.7
"	0.025	0.050	6747	3.2	3.2	3.2

Temperature coefficient.—The temperature coefficient (35° - 25°) of the reaction is very small, being of the order 1.02-1.12 in the wave-lengths in which the reaction was carried out.

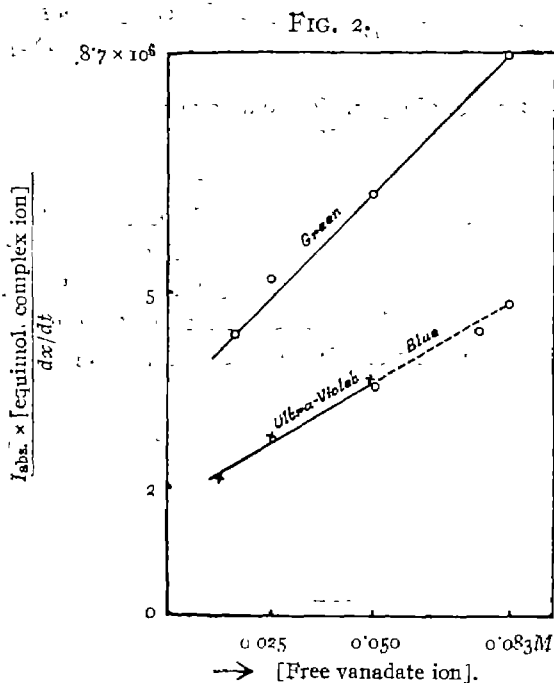
Quantum Efficiency of the Process.—The quantum efficiency of the photo-process in the various wave-lengths is given below :

TABLE XV.

Temp. = 28° . $p_H = 5.2$.

Conc. of H_2T .	Conc. of $NaVO_3$.	Quantum efficiency (η).		
		3130Å	4360Å	5460Å
0.050 M	0.100 M	0.44	0.31	0.14
0.025	0.050	0.28	0.22	0.09
0.017	0.035	0.22	0.17	0.07

The value of γ decreases with increasing wave length of the radiation; and for the same wave length, it decreases with decreasing equimolar concentration.



DISCUSSION.

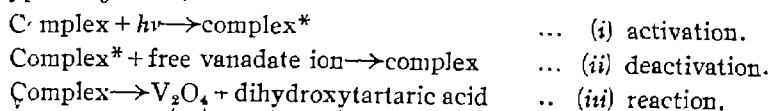
The photoreduction of mixtures of sodium vanadate and tartaric acid, at p_H greater than 4, has the following characteristic features:

(i) The velocity of the reaction decreases with decrease in the concentration of the equimolar complex ion. (ii) The temperature coefficient is small. (iii) The quantum efficiency varies between 0.44 and 0.07. (iv) The velocity of the reaction is proportional to the intensity of the absorbed

radiation. (v) $\frac{I_{\text{abs.}} \times \text{conc. of equimolar complex ion}}{dx/dt}$ when plotted against

concentration of free vanadate ion gives a straight line (Fig. 2).

The following mechanism can explain the main features of the photoreduction: (The term 'complex' refers to an equimolar complex ion of the type $\text{VO}_3^- \cdot \text{HT}^-$).



If k_1 , k_2 and k_3 are the velocity constants for the processes (i), (ii) and (iii) respectively, we have, for the velocity of the reaction the equation,

$$dx/dt = I_{abs} \times \frac{k_1 \times \text{conc. of equimolar complex ion}}{1 + [(k_2/k_3) \times \text{conc. of free vanadate ion}]},$$

i.e.
$$\frac{I_{abs} \times \text{conc. of equimolar complex ion}}{dx/dt}$$

when plotted against concentration of free vanadate ion should give a straight line, as is actually the case. There is good agreement between the observed values of the velocity and those calculated from the above equation, wherein k_1 , and k_2/k_3 have the values given in the above tables

The author wishes to express his thanks to Prof. J. C. Ghosh, for his kind interest and valuable suggestions during the investigation.

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Received June 3, 1941.

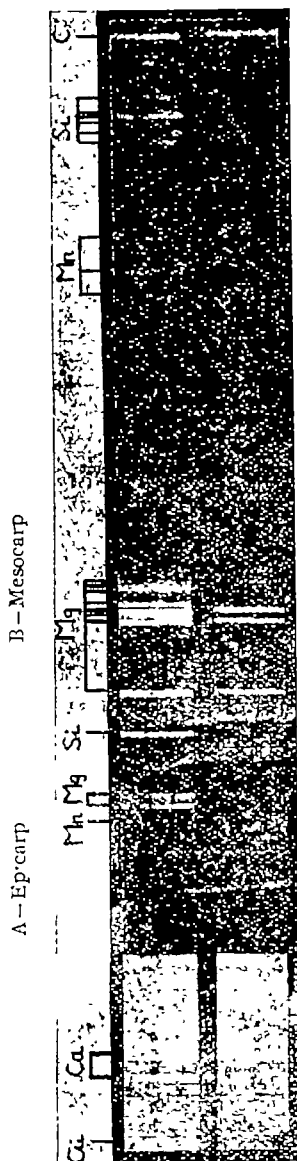
SPECTRUM ANALYSIS OF MINERAL CONTENTS OF FRUITS.

BY L. SIBAIYA AND M. S. VENKATASUBBA RAO.

Using a high frequency spark discharge of the type employed by Walther and Werner Gerlach in their study of biological specimens, the mineral contents of mangoes, plantains, grapes, oranges and apples have been investigated spectroscopically. It has been shown that in the epicarp, mesocarp and endocarp of the same fruit the mineral contents are different, and the conclusion is drawn that generally the outer covering of a fruit is richer than the interior in calcium, magnesium, manganese and silicon.

In recent years the use of the spectrograph in the field of chemical analysis, both qualitative and quantitative, has opened up new avenues of research. As a result of the investigations carried out in many laboratories, it is now clear that the amounts of the minor metallic elements in a given sample can be estimated without recourse to special apparatus. The accuracy of the determination is, however, subject to rather a wide variation, though even in unfavourable circumstances, one can easily distinguish between 0.01, 0.1 and 1%. As a balance against this latitude in accuracy, the estimation is rapid, and a permanent record of the mineral content is obtained. There are in practice several methods of exciting the material under investigation to radiate. The Lundegardh's flame spectrum method of quantitative spectrographic analysis has been principally employed for successful analysis of solutions and soils. Other methods such as the electric arc or the high tension spark are also available for qualitative as well as quantitative analysis. Sundara Rao using treated samples in the arc has examined spectroscopically some fertile and infertile sugarcane soils (*Proc. Indian Acad. Sci.*, 1937, **VI B.**, 91); the fertility of the soil has been traced to minute traces of zinc, manganese and titanium. Representative types of cereals, pulses and leafy vegetables have also been spectroscopically examined by the same author (*Science & Culture*, 1938, **4**, 362; *J. Indian. Chem. Soc.*, 1940, **17**, 351) for trace elements. By discovering new methods of exciting radiation, practically any substance may be subjected to spectroscopic analysis. In attempts to identify the mineral content in organic substances, the carbon arc method is unsuitable on account of the difficulty in obtaining pure carbon rods free from metallic traces. The Lundegardh's flame method is equally inapplicable if the organic substance is to be examined directly without further treatment. The high frequency method of discharge gives an intense source free from

such disadvantages. The high frequency source employed by Walther



and Werner Gerlach ("Clinical and Pathological Applications of Spectrum Analysis" Eng. Ed., Adam Hilger Ltd.) for the analysis of biological specimens, like skin, gallstones, bones etc.. is eminently suited for the examination of all organic matter. Spectroscopic methods have been employed for the analysis of biological fluids for heavy metals (Armstrong and Brackett, *J. Ind. Hyg. Toxicol.* **21**, 446) for determining the magnesium content in blood in various diseases (Zimmer, *Spectrochim. Acta*, 1939, **1**, 93) for finding the metallic nutritional requirements of yeast (Richards and Trontman, *J. Bact.*, 1940, **39**, 739) and allied problems. In the present investigation the mineral contents of the different parts of a number of fruits have been investigated by the high frequency spark method; this method can also be used with success in the case of soils, salts, metal foils, metal deposits and ores.

EXPERIMENTAL.

Both the high and the low frequency currents traverse the spark gap when the ordinary condenser arrangement is employed. The spark gap system was arranged so as to eliminate the low frequency oscillation by means of a small capacity in series. The metallic deposit on one side of a glass plate was connected to one terminal of the secondary of a Tesla transformer and the other terminal connected to a platinum wire (0.2-0.8 mm. thick). The fruit material which was being examined was placed

on the unmetallised side of the glass plate with the platinum wire tip only a few millimetres above the specimen. The radiation from the spark was focussed by a quartz lens on to the slit of a Hilger quartz spectrograph. Using hypersensitive panchromatic plates, intense spectra between 7000 and 2000 Å were recorded with exposures of the order of one minute. The fruit and the skin sections were freshly obtained each time and po

previous treatments were given. The specimen was placed on a filter paper moistened with a 10% sodium nitrate solution and during the exposure the occasional addition of this solution prevented the burning of the sample. When the spark had consumed the portion directly below the electrode, the specimen could be moved so as to bring the other parts into the discharge. Several varieties of mango, orange, apple, grape and plantain were examined. In each case the epicarp (skin) and mesocarp (fruit) have been separately studied. In a few cases the endocarp (seed) has also been subjected to spectroscopic examination.

Various methods have been employed in quantitative spectrum analysis. For instance, in the method due to Lockyer the amount of the element is estimated by the "length" of a spark line. The progressive disappearance of certain lines or the order of their "persistence" as a method in analysis was introduced by Hartley. The method of estimating the abundance by relative intensities of lines, estimated either visually or photometrically, introduced first by de Grammont is widely employed.

In the present work the relative estimates of an element in the various parts of a fruit are given on the basis of the order of "persistence" of the lines of the element in the various spectra as well as of the eye estimates of the relative intensities of the lines employing the "internal standard method". The determination of the abundance of the elements by the order of "persistence" of lines is made with the aid of the data supplied by Twymann ("Wavelength Tables for Spectrum Analysis") and by Smith ("Visual Lines for Spectrum Analysis"). As sodium nitrate solution was employed for rendering the spark gap conducting as

TABLE I.

Mango (*Mangifera indica*, Linn.).

Varieties examined Mulgove, Rasapuri, Neelam, Tootapuri. (Fig. 1).

	Conc. of element % by wt			Remarks
	Epicarp.	Mesocarp	Endo- carp.	
Ca	>0.1	0.01	0.1	{ In Tootapuri (skin) Ca content is less than the figure given here.
Cu	0.001	—	—	Cu is absent in Tootapuri and in Neelam.
Mg	0.1	0.01	0.1	
Mn	0.005	—	—	{ In varieties other than Mulgova Mn con- tent is less than the figure given.
Si	0.1	—	—	{ Si content is higher in Mulgova than in other varieties.
Sr	0.01	—	—	

well as for cooling the specimen, sodium has not been included in the list of elements. Using dilute hydrochloric acid or potassium nitrate solution, however, the abundance of sodium could be estimated. Further work is in progress and from the preliminary results so far obtained, we are giving below only the abundance of those elements which exist to the extent of 0.001 or higher percent. In all the tables concentration refers to percentage by weight.

TABLE II.

Orange (*Citrus aurantium*, Linn.)
Variety—Cooig.

	Conc. of element Epicarp	Skin cover- ing mesocarp.	Mesocarp.
Ca	>0.01	0.01	>0.001
Cu	—	0.001	—
Mg	0.1	0.1	<0.1
Sr	0.01	0.001	—

TABLE III.

Apple (*Pyrus malus*, Linn.)
Variety—Bangalore.

	Conc. of elements. Epicarp	Mesocarp.
Ca	0.001	<0.001
Mg	0.01	0.001

TABLE IV.

Grape (*Vitis vinifera*, Linn.)
Varieties—Black and Kabul.

	Conc. of elements. Epicarp.	Mesocarp.
Ca.	>0.01	>0.001
Cu.*	0.001	—
Mg	0.1	<0.1
Sr	0.001	—

* Cu is present only in Kabul variety and not in black variety.

TABLE V

Plantain (*Musa paradisiaca* Linn.)

Varieties examined—Rasabale,
Pacchabale, and Rajabale.

	Conc. of elements Epicarp	Mesocarp.
Ca †	0.001	<0.001
Mg ‡	0.001	<0.001
Si	0.1	—

† In Rajabale (skin) Ca content is higher than in other variety.

‡ In Rasabale (fruit) Mg content is higher than in other varieties.

On the basis of the above figures it must be concluded that in the fruits examined calcium, magnesium and silicon contents are generally higher in the epicarp than in the mesocarp.

BASE EXCHANGE OF MERCURIC IONS ADSORBED ON WOOL.

BY C. S. NARWANI AND G. T. GURSAHANI.

In addition to chemical reaction of mercuric chloride with wool in the carroting process the adsorption of Hg ions have also been established by observations in the base exchange experiments.

While studying the action of HgCl_2 solutions of various concentrations in 0.1N-HCl on Merino sheep wool and hair to explain the nature of reactions involved in the mercuric carroting of wool for increasing the felting power of fibres, Speaksman and Coke (*Trans. Faraday Soc.*, 1939, **35**, 246) concluded that at temperatures lower than 40° combination of Hg occurred chiefly with the arginine and lysine side-chains. They also found that deaminated wool had affinity for mercuric chloride and they attribute this either to the presence of nitroso groups and the formation of chelate compounds or to the combination with $-\text{NH}-$ groups of the side-chains or of the peptide linkages.

The object of the present work was to examine if chemical combination of HgCl_2 with NH_2 and $-\text{NH}-$ groups of the body proteins as suggested by Seth (*Biochem. J.*, 1923, **17**, 613) can account for the total amount of Hg^{++} ions combined or there was any adsorption occurring simultaneously. Carder and Coffindaffer (*J. Amer. Med. Assoc.*, 1923, **88**, 448) have attempted to establish the adsorption of Hg ions on body proteins of dogs from the removal of its poisonous effect by previous intravenous and intraperitoneal injections of NaCl solution. They explain this effect due to the exchange of Hg^{++} ions with Na^+ ions. The authors have performed base exchange experiments with various chlorides and sulphates having mono- and divalent cations, on sheep wool (Sind desert sheep), treated with various solutions of HgCl_2 in 0.025N-HCl solutions and established adsorption of Hg^{++} ions in addition to chemical reaction. Various cations tried have been arranged in lyotropic series in accordance with their base-exchange capacities for Hg^{++} ions.

EXPERIMENTAL.

Mercuric chloride solution (0.200M) was prepared in 0.025N-HCl (to avoid hydrolysis) by use of Merck's extra pure mercuric chloride. The wool was washed several times in boiling distilled water, dried in the sun under cover and preserved in CaCl_2 desiccator. The mercury was estimated by the gravimetric method, used by Speaksman and Coke (*loc. cit.*) by precipitation as HgS . All experiments were performed in an air thermostat at $35^\circ \pm 0.2^\circ$.

It was experimentally found that with the same molality of HgCl_2 , but different normality of HCl ($0.025N$ - $0.2N$) the total quantity of Hg^{++} ions taken up 1 g. of wool decreases with the increase in concentration of HCl ; the difference between total Hg taken up in case of $0.2M$ - HgCl_2 in $0.2N$ - and $0.1N$ - HCl respectively is about 68% ; so the least acidity viz. $0.025N$ required for avoiding the hydrolysis of HgCl_2 was kept constant in all the experiments.

It was also experimentally found that the maximum amount of Hg^{++} ions adsorbed on 1 g. of wool exchanged with 150 c.c. of $0.2N$ - NaCl ; higher concentrations of NaCl exchange the same quantity of Hg^{++} ions as $0.2N$. So $0.2N$ solutions of the salt were used in all base-exchange experiments.

TABLE I.

Influence of time.

Wool = 1 g. HgCl_2 solution ($0.05M$ in $0.025N$ HCl) = 150 c.c.

Time.	Initial.	Conc. of HgCl_2	Final.	Hg taken up by 1g. of wool
1 hr.	$0.050 M$		$0.0449 M$	0.1511
8	0.050		0.0447	0.1583
16	0.050		0.0446	0.1635
24	0.050		0.0444	0.1684
32	0.050		0.0442	0.1734
40	0.050		0.0441	0.1784

Influence of initial concentrations of HgCl_2 on the adsorbed and reacted quantity was also studied. Wool (1 g.) was immersed in 150 c.c. of HgCl_2 solutions of various concentrations made in $0.025N$ HCl contained in Jena glass-stoppered bottles for 24 hours in an air thermostat at 35° . The solution was then decanted off and 25 c.c. analysed for Hg^{++} ions. The results are shown in Table II. The wool was washed with cold CO_2 -free distilled water five times, using 30 c.c. at a time. The water was drained out from the wool by pressing it with flat glass rod. The wool was then immersed in 150 c.c. of $0.2N$ - NaCl for 24 hours at 35° , the solution was decanted and 75 c.c. analysed for Hg^{++} ions and the total quantity taken out by NaCl was calculated. Assuming this quantity of Hg^{++} ions to be adsorbed, it was deducted from the total quantity taken up to obtain the quantity reacted. The results are shown in Table II.

TABLE II.

Conc. of HgCl_2 Initial.	Final.	Total Hg taken up.	Hg taken out by NaCl	Hg remaining behind.
0.0250 M	0.0214 M	0.1094 g	0.0731 g.	0.0363
0.0500	0.0444	0.1684	0.1035	0.0649
0.1000	0.0915	0.2567	0.1649	0.0918
0.1500	0.1373	0.3819	0.2204	0.1615
0.2000	0.1845	0.4656	0.2732	0.1924

In order to compare the base-exchange capacities of various cations and anions, wool (1 g.) immersed in 150 c.c. of 0.05M- HgCl_2 solution in 0.025N HCl for 24 hours at 35°. was washed and treated with 150 c.c. of 0.1N- and 0.2N solutions of various salts for 24 hours at 35° and the exchanged quantity of Hg^{++} ions determined in the same manner as shown above. The results are shown in Table III.

TABLE III.

Total Hg before treatment = 0.1684 g.

Salt used.	Hg exchanged		Hg remaining	
	0.1N.	0.2N.	0.1N.	0.2N.
KCl	0.0893 g.	0.1066 g	0.0791	0.0618
NH_4Cl	0.0863	0.1045	0.0801	0.0639
NaCl	0.0862	0.1035	0.0822	0.0649
CaCl_2	0.0946	0.1045	0.0738	0.0639
BaCl_2	0.0931	0.1032	0.0753	0.0652
MgCl_2	0.0879	0.0966	0.0805	0.0718
K_2SO_4	0.1181	0.1181	0.0503	0.0503
$(\text{NH}_4)_2\text{SO}_4$	0.1164	0.1164	0.0520	0.0520
Na_2SO_4	0.1121	0.1121	0.0563	0.0563
MgSO_4	0.1131	0.1131	0.0553	0.0553

DISCUSSION.

Table I shows that the total quantity of Hg taken up by 1 g. of wool at first increases quickly and after 1 hour slowly and regularly with time; this proves that there is a chemical reaction between HgCl_2 and wool, because the velocity of adsorption is very great in view of the time intervals;



for the experiments in case of a true solution Lenard (*Sitzungsber. Dent. Akad. Heidelberg*, 1914, **5A**, 28) assumes a period of 1/100 second to 1 second for the setting of equilibrium up to 95%.

From Table II it appears that there is diversion at equilibrium concentration corresponding to 0.1M initial concentration of HgCl_2 both in the cases of total Hg taken up and the Hg remaining behind after treatment with 0.02N-NaCl, but there is no such break in case of the curve for Hg^{++} taken out by NaCl; this shows that there is adsorption of Hg^{++} ions in addition to the reaction of Hg^{++} ions with wool. The adsorption curve is not a regular parabola, since on plotting $\log x/m$ against $\log c$, it was found that a straight line is not obtained. On the assumption of the reaction of Hg^+ (remaining behind) with the wool, the reaction curve, obtained by plotting this against equilibrium concentration of HgCl_2 , shows that there are two types of reactions as concluded by Spackman and Coke (*loc. cit.*).

Table III shows that the cations of the same valency possess different base-exchange capacities for Hg^+ ions adsorbed on wool and follow the order $\text{K} > \text{NH}_4 > \text{Na}$ in case of monovalent ions and $\text{Ca} > \text{Ba} > \text{Mg}$ in case of divalent ions. Compared amongst themselves the order followed by cations is $\text{K} > \text{NH}_4 > \text{Ca} > \text{Na} > \text{Ba} > \text{Mg}$ in case of chlorides and $\text{K} > \text{NH}_4 > \text{Mg} > \text{Na}$ in case of sulphates. If the sulphates and chlorides with the same cations are compared it is found that sulphates have more base-exchange capacity than chlorides.

The above observations definitely lead to the conclusion that there is adsorption of Hg ions on wool in addition to chemical reactions of HgCl_2 .

The authors take the opportunity of thanking Dr. J. V. Lakhani, Head of the Chemistry Department, for giving facilities for this work.

RHYTHMIC PRECIPITATION OF SILVER CHLORIDE IN GELATIN TANNED WITH CHROMIUM CHLORIDE.

BY C. S. NARWANI AND G. T. GURSAHANI.

On allowing a highly concentrated silver nitrate solution to diffuse into a gelatin gel, tanned with CrCl_3 of such concentrations that all the available Cl' is combined with the gelatin, in a test tube, dirty white rings of AgCl have been obtained. The study of the influence of concentration of gelatin, CrCl_3 , and AgNO_3 on the dimensions of the rings and interspaces shows that they behave differently from those of $\text{Ag}_2\text{Cr}_2\text{O}_7$ rings in gelatin mixed with $\text{K}_2\text{Cr}_2\text{O}_7$.

Up to this time the reaction studied with regard to Liesegang rings are such that the reacting ion in the gel is quite free and not in any way bound up with the gel substance. The abnormal behaviour of chrome-tanned gelatin with regard to its solubility and muta-rotation as observed by Kuntzel and Boensel (*Collegium*, 1936, 576) throwing reflection on the theory of tanning of hides and adsorption experiments by Cameron and McLanlyhlin (*J. Phys. Chem.*, 1937, 41, 961) show that both the cations and anions of chromium salts become chemically combined with gelatin.

Object of the present work is to see how the Cl' ion of CrCl_3 , supposed to be chemically combined with gelatin molecule, influences the formation of silver chloride layers when a highly concentrated silver nitrate solution is diffused in the gelatin tanned with dilute chromium chloride. The authors have studied the influence of change of concentrations of chromium chloride, silver nitrate and gelatin on the nature and width of the silver chloride rings as well as their interspaces.

EXPERIMENTAL.

The preliminary experiments revealed the conditions and the relative concentrations of gelatin, CrCl_3 , and AgNO_3 suitable for obtaining the rings at 25° (Table I). The concentrations of CrCl_3 chosen were such as may contain Cl' just sufficient to combine with gelatin taken in each test tube.

TABLE I.

Gelatin.	CrCl_3	AgNO_3 .	Minimum age of gel.	Minimum time for rings to develop.
20 c.c. of 3 to 4.5%	1 c.c. of 5% to 7%	5 c.c. of 4 to 6%	24 hours	11 days.

Occasional exposure to day light for a few minutes only was also found to be essential in addition.

Test tubes of the same dimensions were used for the formation of AgCl rings. Gelatin solution (20 c.c.) was introduced in a test tube and CrCl₃ solution (1 c.c.) of the required concentration added to it and mixed well by shaking; the mixture was allowed to set to a gel in an air thermostat at 25°(±1°) for 24 hours. The required AgNO₃ solution (5 c.c.) was then poured at the top of gel along the side of the test tubes taking care not to disturb the gel. All the test tubes were allowed to remain in the rack in the air thermostat free from light for eleven days. Every alternate day, day light was admitted into the thermostat for five minutes. After eleven days a set of three test tubes was taken out each time carefully and immediately photographed after placing in a rack kept at a fixed distance from the camera.

The combining weights of gelatin as a base as well as an acid, determined by conductometric titration of a 5% solution of gelatin against N-HCl and N-NaOH respectively, were found to be 1111 and 1428 respectively; from this the quantities of Cl^I and Cr^{III} in combination with gelatin as well as in the free state were calculated (Tables II and III).

TABLE II.

Gelatin.	Cl ^I available in tubes (containing CrCl ₃ , 10H ₂ O).			Cl ^I required for combination
	7%.	6%.	5%.	
3.0%	0.0220 g.	0.0189 g.	0.0157 g	0.0192 g
3.5	"	"	"	0.0224
4.0	"	"	"	0.0256
4.5	"	"	"	0.0288

Free Cl^I in case of 3% gelatin might be present in the form of HCl, since CrCl₃ may be getting hydrolysed to Cr(OH)₃ and HCl, the former being colloiddally adsorbed on the gel.

TABLE III.

Gelatin.	Cr ^{III} available in tubes (containing CrCl ₃ , 10H ₂ O)			Cr ^{III} required for combination.
	7%.	6%.	5%	
3.0%	0.0108 g.	0.0092 g.	0.0077 g.	0.0073 g.
3.5	"	"	"	0.0085
4.0	"	"	"	0.0097
4.5	"	"	"	0.0109

A comparison of Tables II and III reveals that Cr^{+++} is free in such test tubes as contain no free Cl' ; in such cases Cr might be present as $\text{Cr}(\text{OH})_3$.

DISCUSSION.

On allowing a highly concentrated AgNO_3 solution to diffuse into a gelatin gel, tanned with CrCl_3 of such concentrations that all the available Cl is combined with the gelatin in a test tube, dirty white rings of AgCl and black brown spaces, quite distinct from the chrome-tanned gel, have been obtained in the lower zone of the precipitate.

The points worth noting in our case are (i) that the interspaces between the rings and the width of the ring itself go on decreasing in downward direction; (ii) the width of the ring increases and interspaces decrease with decrease in concentration of gelatin; (iii) interspaces, however, increase with increasing concentration of AgNO_3 and decrease with increasing concentration of CrCl_3 .

The above observations show that rhythmic precipitation of AgCl in gelatin tanned with CrCl_3 takes place in quite a different manner from that of $\text{Ag}_2\text{Cr}_2\text{O}_7$ in gelatin mixed with $\text{K}_2\text{Cr}_2\text{O}_7$. In both cases nearly the same concentrations of gelatin and AgNO_3 have been found suitable for producing the rings. The principal points of difference between the two cases appear to be (i) that the Cr_2O_7 ions reacting with AgNO_3 remain free, while the Cl' ions in this case remain almost totally in combination with gelatin (*cf.* Table III); (ii) that the structure and physical properties of gel in tanned conditions are different from those in ordinary state as observed by Kuntzel and Boensel (*loc. cit.*). But since Gore (*Kolloid Z.*, 1936, **76**, 193) has been able to get rhythmic precipitation in non-gelatinous media such as $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ precipitates, the responsibility of the change in the structure of the gel in such abnormal behaviour of AgCl rings, is therefore, ruled out.

It has been noted above that after occasional short exposure to daylight, the colour of the interspace in our case was brown black, quite different from that of chrome-tanned gel, and that on continuous exposure to day light the colour of rings and interspaces became uniform; from this we conclude that in our case a layer of coagulated AgCl is followed by a layer of peptised AgCl , as observed by Dhar and Chatterji (*J. Phys. Chem.*, 1924, **28**, 41) in case of mercuric iodide rings. The authors feel that gelatin chloride gets partially ionised at lower p_{H} value (3.4) as observed

by Hitschock (*J. Gen. Physiol.*, 1922, **235**, 383); Sokolon and Kaja (*Kolloid Z.*, 1935, **70**, 314) have found that when chromium salts combine with gelatin p^{H} value falls rapidly. Since only free Cl' ions migrate upwards to meet the diffusing AgNO_3 , while combined chloride remains bound in the molecule, no space in the gel is totally free from chloride and hence the clear gel does not succeed the precipitated layer. The AgNO_3 reacting with free Cl' ions forms AgCl sol, while that reacting with free Cl' ions forms AgCl precipitate. But until AgNO_3 solution reaches a high dilution on diffusion, AgCl sol is coagulated by AgNO_3 ; hence the ring formation of AgCl takes place in the lower zone of the precipitate.

The authors express their thanks to Dr J. V. Lakhaní, Head of the Chemistry Department, for giving facilities for this work.

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Received July 15, 1941.

ADSORPTION OF HYDROXYBENZENES BY SUGAR CHARCOAL DISCONTINUITIES IN THE ADSORPTION OF PHENOL, RESORCINOL, AND QUINOL FROM AQUEOUS SOLUTIONS

BY KESHO DASS JAIN AND J. B. JHA

Adsorption by sugar coal of phenol, resorcinol and quinol from aqueous solutions have been studied.

In continuation of our previous work (Jain and Jha, *J. Indian Chem. Soc.*, 1940, 17, 685), adsorption of hydroxybenzenes by sugar charcoal has been further studied.

EXPERIMENTAL.

The adsorption experiments were carried out by weighing exactly 0.5 g. of the charcoal in clean, dry, glass bottles similar in size to which 100 c.c. of each solution in freshly prepared distilled water was pipetted separately. The bottles were shaken for the same length of time and kept for about 24 hours, at the end of which interval the amount of solute was determined in the supernatant liquid by the bromine method (Redman, Weith and Brock, *J. Chem. Soc. Abst.*, 1913, I, 632) in the case of phenol, cresols (Chausser, *Chem. Zentral.*, 1900, II, 118), and resorcinol.

An approximately 0.1N brominating solution was prepared by dissolving 2.76 g. of potassium bromate and 15 g. of potassium bromide in water, and making up the solution to one litre. The brominating solution was standardised by means of a standard sodium thiosulphate solution.

15 C.c. of each of the solutions of the said substances (about 0.1N), were placed in a stoppered bottle together with 50 c.c. of water and 5 c.c. of HCl ($d_{1.2}$); the brominating solution was now run in from a burette and the bottle shaken continuously until a slight yellow colour was permanent. The bottle was stoppered and after shaking for 1 minute, 0.5 c.c. of a 20% solution of potassium iodide was added, the mixture shaken for another minute and the iodine titrated with standard thiosulphate solution.

Estimation of Quinol.—The supernatant liquid of quinol was titrated with iodine according to the method of Kolthoff (*Rec. trav. chim.*, 1926, 45, 745): 0.4 C.c. of 4N-acetic acid, about 8 c.c. of 2N sodium acetate, and an excess of standard iodine solution were added to 10 c.c. of about 0.1N-quinol solution and the mixture was titrated back with standard sodium thiosulphate. A 0.00001N solution can thus be titrated to 1%.

Blank experiments were run side by side to determine the original concentration (C_e). Determination with charcoal gave the equilibrium

concentration. The amount of adsorption (X) was determined by difference ($C_0 - C_e$) from 100 c.c. of the aqueous solution. Equilibrium concentrations were calculated in millimoles per litre.

RESULTS.

The results for the adsorption of phenol and cresols are recorded in Table I, while that of dihydroxybenzenes in Table II, and in Fig. 1.

TABLE I.

Adsorption by 0.5 g. sugar charcoal from 100 c.c. of aqueous solutions.

Phenol.					
C_0 .	C_e .	X .	X/m .	$\log C_e$.	$\log X/m$.
0.4414	0.3853	0.0561	0.1122	1.5858	1.0500
0.4193	0.3604	0.0589	0.1178	1.5568	1.0712
0.3972	0.3382	0.0590	0.1180	1.5292	1.0719
0.3752	0.3137	0.0615	0.1230	1.4965	1.0899
0.3531	0.2946	0.0585	0.1170	1.4692	1.0682
0.3310	0.2721	0.0589	0.1178	1.4348	1.0712
0.3090	0.2485	0.0605	0.1210	1.3954	1.0828
0.2870	0.2275	0.0595	0.1190	1.3570	1.0755
0.2439	0.1841	0.0598	0.1196	1.2650	1.0778
0.2252	0.1638	0.0614	0.1228	1.2144	1.0892
0.2139	0.1534	0.0605	0.1210	1.1858	1.0828
0.2026	0.1381	0.0645	0.1290	1.1402	1.1106
0.1914	0.1345	0.0569	0.1138	1.1287	1.0561
0.1813	0.1238	0.0575	0.1150	1.0927	1.0607
0.1689	0.1143	0.0546	0.1092	1.0581	1.0382
0.1576	0.1041	0.0535	0.1070	1.0175	1.0294
0.1464	0.0947	0.0517	0.1034	0.9763	1.0145
<i>p</i> -Cresol.					
0.3742	0.3541	0.0201	0.0402	1.5491	2.6042
0.3555	0.3344	0.0211	0.0422	1.5242	2.6253
0.3368	0.3148	0.0220	0.0440	1.4980	2.6435
0.3181	0.2949	0.0232	0.0464	1.4696	2.6665
0.2994	0.2756	0.0238	0.0476	1.4402	2.6776
0.2806	0.2556	0.0250	0.0500	1.4076	2.6990

TABLE I (contd.).

<i>m</i> -Cresol.					
C_0	C_e	X	X/m	$\text{Log } C_0$	$\text{Log } X/m$
0.4131	0.3891	0.0240	0.0480	1.5900	2.6912
0.3925	0.3674	0.0251	0.0502	1.5652	2.7007
0.3721	0.3467	0.0254	0.0508	1.5400	2.7059
0.3515	0.3255	0.0260	0.0520	1.5126	2.7160
0.3309	0.3034	0.0265	0.0530	1.4820	2.7243
0.3103	0.2830	0.0273	0.0546	1.4518	2.7372
<i>o</i> -Cresol					
0.4093	0.3813	0.0280	0.0560	1.5812	2.7482
0.3780	0.3481	0.0299	0.0598	1.5414	2.7767
0.3522	0.3213	0.0309	0.0618	1.5073	2.7910
0.3284	0.2971	0.0313	0.0626	1.4729	2.7966
0.3045	0.2721	0.0324	0.0648	1.4348	2.8116
0.2826	0.2498	0.0328	0.0656	1.4076	2.8169

TABLE II.

Dihydroxybenzenes.

Adsorption of dihydroxybenzenes by 0.5 g. charcoal from 100 c.c. aqueous solution.

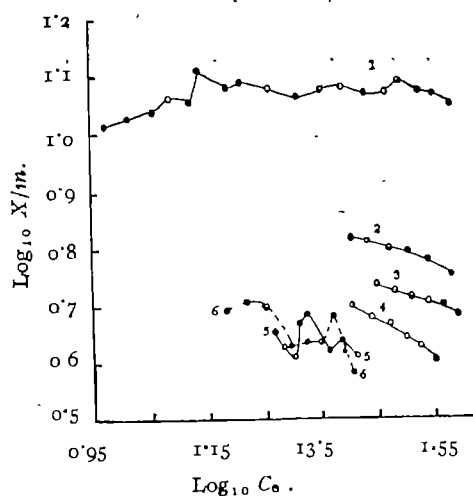
Hydroquinone.					
C_0	C_e	X	X/m	$\text{Log } C_0$	$\text{Log } X/m$
0.2740	0.2550	0.0190	0.0380	1.4065	2.5798
0.2603	0.2364	0.0239	0.0478	1.3736	2.6794
0.2466	0.2249	0.0217	0.0434	1.3521	2.6375
0.2329	0.2112	0.0217	0.0434	1.3247	2.6375
0.2192	0.1977	0.0215	0.0430	1.2960	2.6335
0.2055	0.1805	0.0250	0.0500	1.2565	2.6990
0.1918	0.1662	0.0256	0.0512	1.2206	2.7093
0.1781	0.1533	0.0248	0.0496	1.1856	2.6955

TABLE II (contd.).

Resorcinol.					
C_e	C_e	X	X/m	$\text{Log } C_e$	$\text{Log } X/m$
0.2777	0.2573	0.0204	0.0408	1.4104	2.6107
0.2639	0.2421	0.0218	0.0436	1.3840	2.6395
0.2501	0.2293	0.0208	0.0416	1.3604	2.6191
0.2363	0.2120	0.0243	0.0486	1.3263	2.6866
0.2294	0.2060	0.0234	0.0468	1.3139	2.6702
0.2225	0.2020	0.0205	0.0410	1.3051	2.6128
0.2165	0.1950	0.0215	0.0430	1.2900	2.6335
0.2087	0.1861	0.0226	0.0452	1.2697	2.6551

Table III shows that the adsorption isotherms of the following substances are of somewhat periodic type,

FIG. 1.



Curves 1-6 refer respectively to phenol
o-cresol, *m*-cresol, *p*-cresol, resorcinol
 and quinol.

TABLE III.

Molar conc. at the max. and min points on the curve.	Diff. bet. two max. & min. pts.	Molar conc. at the max & min. points on the curve.	Diff. bet. two max. and min. pts.	Molar conc at the max and min. points on the curve	Diff. between two max and min. pts
Phenol.				Quinol.	
0'00409	—	0'00243	0'00021	0'00231	
0'00382	0'00027	0'00201	0'00042	0'00214	0'00017
0'00361	0'00021	0'00174	0'00027	0'00180	0'00034
0'00334	0'00027	0'00163	0'00011	0'00151	0'00029
				Resorcinol.	
0'00313	0'00021	0'00146	0'00017	0'00234	
0'00291	0'00022	0'00143	0'00003	0'00220	0'00014
0'00264	0'00027	0'00122	0'00021	0'00192	0'00028
				0'00177	0'00015
				0'00170	0'00007

Chaplin (*J. Phys. Chem.*, 1932, **32**, 909) studied the adsorption of aqueous phenol on charcoal and obtained discontinuous curves with rectangular steps. Koltzoff and van der Goot (*Rec. trav. chim.*, 1929, **48**, 265, 287) found that in the adsorption of hydroxybenzenes on charcoal Freundlich adsorption equation could be satisfactorily applied to the results.

The authors are thankful to Professors H. Krall and B. L. Vaish for their kind interest in this work.

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Received June 3, 1941.

THE MAGNETIC SUSCEPTIBILITIES OF METALLIC OXIDES AND THEIR MOLECULAR STRUCTURES WITH SPECIAL REFERENCE TO THOSE OF COBALT.

BY S. S. BHATNAGAR, BRAHM PRAKASH, AND MOHOMMED ABDUL QAYYUM.

Magnetic susceptibility values of different samples of cobaltous, cobaltous and cobaltic oxides, prepared in different ways, have been measured. The observed values of μ_B have been utilised to discuss the molecular constitution of the cobalt oxides.

The measurement of magnetic properties of compounds has been extensively employed to establish their constitution. No systematic attempt, however, has been made to investigate the magnetic properties of metallic oxides. Different workers report widely divergent results of the magnetic susceptibilities of the oxides of transition metals and there are few precise determinations of the variation of χ with temperature.

Thus in literature the values of the susceptibility of chromic oxide are given by Meyer (*Ann. Physik*, 1899, **68**, 325; **69**, 236) as 24.0×10^{-6} ; Moles and Gonzales (*Annal. Fis. Quim.*, 1923, **21**, 204) as 26.7×10^{-6} ; Wedekind and co-workers (*Ber.*, 1915, **48**, 105) as 25.97×10^{-6} and Huttig (*Z. Elektrochem.*, 1933, **39**, 368) as varying between 28 to 47×10^{-6} . For the susceptibility of chromium dioxide, Moles and Gonzales (*loc. cit.*) gave a value of 42.2×10^{-6} , while Albercht and Wedekind (*Z. anorg. Chem.*, 1933, **210**, 105) reported a value of 36.0×10^{-6} . Further the value of χ obtained by Wedekind and Horst (*Ber.*, 1915, **48**, 105) for manganous oxide was 56.16×10^{-6} , for manganous oxide 65.5×10^{-6} and for manganese dioxide 46.58×10^{-6} , whereas Theodorides (*Compt. rend.*, 1920, **171**, 948) found 67.46×10^{-6} as the χ value for manganous oxide, Feytis (*Compt. rend.*, 1911, **182**, 710) 74.3×10^{-6} for manganous oxide, Meyer (*loc. cit.*) and Wistrand ("Magnetiska susceptibilitaten hos Kvart, etc." Upsala, 1916) 27.0×10^{-6} and 32.3×10^{-6} respectively for the dioxide. Similarly for vanadium pentoxide, Wedekind and Horst (*Ber.*, 1912, **45**, 262; 1915, **48**, 105) found the magnetic susceptibility value to be 0.16×10^{-6} while Meyer (*loc. cit.*) gave 0.95×10^{-6} and Berkman and Zocher (*Z. physikal. Chem.*, 1927, **124**, 318) 0.39×10^{-6} , and for uranosic oxide, Honda (*Ann Physik*, 1910, **iv**, **32**, 1844) found χ as 4.34×10^{-6} ; while Wedekind and Horst (*loc. cit.*) reported 0.95×10^{-6} . Ferric oxide is usually paramagnetic but also exists in a ferro-magnetic form both in nature and as a synthetic product.

Similar observations have been made for cobalt and nickel oxides, for the latter it has been shown by Bhatnagar and Bal (*J. Indian Chem. Soc.*, 1934, **11**, 603) that traces of metallic nickel present as an impurity account for the anomalous results,

The marked divergence in values of magnetic characteristics of oxide probably reflects their extreme variability in composition and the difficulty of obtaining them in a pure state. Recent work by Bhatnagar, King and collaborators (*J. Chem. Soc.*, 1939, 1433) on the study of the magnetic susceptibilities of chromium and manganese oxides supports this view and they have shown that the differences are due to impurities, in particular, to small amounts of chemisorbed gases.

The present work deals with the oxides of cobalt which have elicited good deal of controversy. While Beetz (*Pogg. Ann.*, 1844, **61**, 472) found cobaltous oxide to be non-magnetic, Williams (*Phys. Rev.*, 1926, *ii*, **26**, 127) reported it as ferromagnetic, Hausknecht ("Magneto-chemische Untersuchungen," Strassburg, 1914, 18) gave 67×10^{-6} for its magnetic susceptibility and Herroun and Wilson (*Proc. Phys. Soc.*, 1921, **33**, 204) 74.5×10^{-6} . In the case of cobaltous oxides Co_2O_3 , Merck and Wedekind (*Z. anorg. Chem.*, 1930, **182**, 49) found $\chi = 32 \times 10^{-6}$ Hausknecht (*loc. cit.*) 34.4×10^{-6} and Herroun and Wilson (*loc. cit.*) 39.6×10^{-6} to 43.6×10^{-6} , whereas Schwarzenberg, (*Annalen*, 1855, **97**, 212) stated that it is non-magnetic. The magnetic properties of cobaltic oxide, Co_2O_3 , have not been studied.

It is clear from this resume that it would be useless to try to elucidate the molecular structure of the cobalt oxides with the help of these controversial χ -values.

It is well known that changes in principal valency bring about changes in magnetic moment which can be correlated with atomic structure. In general, atoms or ions which contain completed sub-groups possess zero or very small magnetic moment and are consequently diamagnetic, whilst those in which the sub-group is incompletely filled are paramagnetic. The magnetic moment in Bohr units is given by

$$\mu_B = g \sqrt{l(l+1)}$$

or $\mu_B = \sqrt{4s(s+1) + l(l+1)}$ which reduces to

$$\mu_B = \sqrt{4s(s+1)}$$

when the orbital moment is fully quenched. An examination of Table I will show that in the salts the experimental values of magnetic moment agree very closely with those calculated on the above formula for spin only.

TABLE I.
Magnetic moments of some metallic salts.

Salt	μ_B		No. of unpaired spins.	Salt.	μ_B		No of unpaired spins.
	Found	Calc.			Found.	Calc.	
CoBr_2	4.92	4.90	4	FeCl_2	5.79	5.92	5
MnCl_2	5.68	5.92	5	CrCl_2	4.90	4.90	4
MnBr_2	5.83	5.92	5	CrCl_3	4.05	3.87	3

The magnetic moment values for the oxides of the metals with completed inner shells are also in good agreement with theory, but with oxides of the transition metals, as will be seen from Table II, there is a wide divergence between the theoretical and the measured values. The divergence between the two values is so great that it makes the magnetic susceptibility method of determining valency a useless means.

TABLE II.

Magnetic moments of some metallic oxides.

Oxides.	μ_B		No. of unpaired spins.	Oxides.	μ_B		No. of unpaired spins
	Found.	Calc.			Found.	Calc.	
MnO	2.78	3.87	3	Cr ₂ O ₃	2.12	3.87	3
MnO ₂	3.72	5.92	5	CrO ₃	0.344	0.00	0
Mn ₂ O ₃	3.53	4.90	4	CoO	2.91	4.9	4
Fe ₂ O ₃	1.96	5.92	5	CuO	0.90	1.73	1
				Cu ₂ O	0.447	0.00	0

It may also be that these divergencies between theory and practice are due to deviations from Curie's law, viz: $\chi_M = C_M / T$. In Curie's law no account is taken of the distortions produced by interatomic forces, and this factor is primarily responsible for the observed divergencies from theory. Weiss modified Curie's law to $\chi_M = C_M / (T - \theta)$, where θ takes cognizance of the molecular distortions. An attempt has been made in the present investigation to see whether the magnetic moments, calculated on the Weiss modification of the law, gives better concordance with theory. The observed values of μ_B have been utilised to discuss the molecular constitution of the cobalt oxides.

EXPERIMENTAL.

The reagents employed in the preparation of the oxides were of A. R. quality and the samples prepared were tested to be free from traces of ferromagnetic impurities. Because of the ease with which oxides adsorb gases, measures were taken to ensure that the samples obtained did not contain adsorbed gases. Before embarking on magnetic and chemical analysis, the samples were heated for prolonged intervals at 100° in *vacuo* and then allowed to cool in vacuum.

The methods of preparation and the results of analyses are as follows.

Methods of Preparation.

Cobaltous Oxide—The specimens prepared by the following six methods have been studied.

(i) *Heating cobalt carbonate in vacuum* (Mobius Method, "Untersuchungen über Cobaltoxyde und deren Systeme mit Sauerstoff," Leipzig, 1929). Cobalt carbonate was heated under vacuum in a silica tube to about 900° in an electric furnace. The product obtained was allowed to cool in *vacuo*. The colour of the oxide was yellowish grey. Cobalt carbonate was obtained by the method of Mobius and others (Mobius, *loc. cit.*, Bertrand, *Jahrb. Miner. Z.* ref. 161; H. de Saurmont, *Ann. chim. phys.*, 1851, 32, 153).

(ii) *Heating cobalt carbonate in carbon dioxide* (Mobius, *loc. cit.*, Russel, *J. Chem. Soc.*, 1863, 16, 61; Winkelblech, *Annalen*, 1835, 113, 148, 253). Cobalt carbonate was electrically heated in an atmosphere of CO_2 to about 900° in a silica tube. The colour of the oxide was yellowish grey.

(iii) *Heating cobaltous hydroxide in CO_2* . (Blanc and Mobius, *Z. physikal. Chem.*, 1929, 142, 151; *Phys. Z.*, 1927, 32, 887, 288) Cobaltous hydroxide prepared according to the method of Huttig and Kassler (*Z. anorg. Chem.*, 1930, 187, 16, 24) was heated electrically in a silica tube to 900° in an atmosphere of carbon dioxide. The oxide obtained was yellowish grey in colour.

(iv) *Oxidising cobalt metal with nitric oxide* (Sabatier and Sanderens's method, *Compt. rend.*, 1892, 114, 1429). Cobalt metal obtained by the reduction of cobaltous oxide, Co_3O_4 , by hydrogen at a temperature of 506° (Wohler and Balz, *Z. Elektrochem.*, 1921, 27, 466) was heated at 150° in a stream of pure and dry nitric oxide gas. The oxide was greyish black in colour.

(v) *Reduction of cobaltic oxide in ammonia* (Vorster, "Ueber die Einwirkung des Ammoniaks auf die Oxyde des Nickel und Kobalt", Göttingen, 1861; Winkler, *J. prakt. Chem.*, 1864, 91, 215). Cobaltic oxide obtained according to Winkelblech's method (*Annalen*, 1835, 13, 148, 253; *J. prakt. Chem.*, 1935, 14, 6, 62) was heated at 350° in a current of dry ammonia. The colour of the oxide was brownish yellow.

(vi) *Reduction of cobaltous oxide with carbon*. (Kalmus's method, *Rep. Canadian Dept. Mines*, 1913, 259, 309; *Ind. Eng. Chem.*, 1914, 6, 115). Cobaltous oxide, prepared by electrically heating cobalt nitrate was heated with 2–3% of sugar charcoal at 900° . A greyish black product was obtained.

Cobaltous Oxide.—Cobaltous oxide was prepared by the following three methods :—

(i) *Heating cobalt nitrate* (Hempel, *Z. anorg. Chem.*, 1896, **11**, 77 ; Remmler, *ibid.*, 1892, **2**, 224). Cobaltous nitrate was first heated in an electric furnace at a low temperature and when the evolution of nitrogen peroxide gas ceased it was calcined at 800° — 900° . The undecomposed nitrate was dissolved in water and the oxide dried.

(ii) *Calcining cobalt oxalate* (Rammelsberg's method, *Pogg. Ann.*, 1849, **78**, 93). Cobalt oxalate was calcined at 900° .

(iii) *Heating a mixture of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ and NH_4Cl* . (Schwarzenberg, *Annalen*, 1825, **97**, 212 ; Zimmermann, *ibid.*, 1886, **232**, 335 ; Gorgen, *Compt. rend.*, 1855, **100**, 175). A mixture of cobaltous chloride and ammonium chloride was heated to 500° in a silica tube. The product was digested with water to dissolve out the soluble salts and the oxide dried.

Cobaltic Oxide.—The following two methods were employed for the preparation of cobaltic oxide.

(i) *Calcination of cobalt nitrate at low temperatures*. (Proust and Winkelblech's method, *J. Phys.*, 1806, **68**, 421). Cobaltous nitrate was calcined at 184° for a long time. The product was powdered and washed well with water, filtered and dried at a low temperature.

(ii) *Oxidising cobalt chloride with potassium chlorate*. (Thompson's method, *Chem. News*, 1863, **7**, 184 ; *Z. anorg. Chem.* 1864, **3**, 375 ; *Technologiste*, 1863, **24**, 337). A concentrated aqueous solution of cobaltous chloride was mixed with one and a half parts of potassium chlorate and was slowly evaporated to dryness. The residue was heated at about 200° and the product so formed was extracted with water to remove soluble salts and finally dried at temperatures below 150° .

Analysis of the Oxides.

Cobalt in the various oxides was determined both by electrodeposition method and by cobalt sulphate method.

The amount of available oxygen in the oxides was determined by the iodine method. A known weight of the oxide was heated with an excess of hydrochloric acid. The chlorine evolved was absorbed in potassium iodide solution and the iodine thus liberated was titrated against standard sodium thiosulphate solution.

The results of these analyses are recorded in Table III.

TABLE III.

Analysis of the oxides.

Oxide samples		C o b a l t		Available oxygen	
		Found.	Calc.	Found.	Calc.
Cobaltous oxide	I	78.589%	78.65%	—	0.000%
"	II	78.56	"	—	—
"	III	78.57	"	—	—
"	IV	79.02	"	—	—
"	V	78.14	"	0.085%	—
"	VI	78.264	"	0.099	—
Cobaltosic	I	73.33	73.43	6.639	6.642
"	II	73.38	"	6.638	"
"	III	73.32	"	6.640	"
Cobaltic	I	71.23	71.08	9.62	9.647
"	II	71.18	"	9.629	"

Magnetic Measurements.

The magnetic susceptibility values of the samples were determined on a modified form of Gouy's magnetic balance (Bhatnagar and Bal, *loc cit.*, Gouy, *Compt. rend.*, 1889, 109, 935). The calculations of χ were made according to the equation,

$$\chi p_2 = \frac{1}{m p_1} \left\{ (\chi p_1 m p_1 - \chi_a m_a p_1) \frac{\omega p_2}{\omega p_1} + \chi_a m_a p_2 \right\}$$

where χp_1 and χp_2 are respectively the specific susceptibilities of the standard substance of the specimen and χ_a is the susceptibility of air, ωp_1 and ωp_2 are the respective pulls, $m_a p_1$ and $m_a p_2$ are the masses of air displaced respectively by the standard substance and by the specimen.

The accuracy of the balance was tested by measuring the magnetic susceptibility of standard paramagnetics.

For measurements of magnetic susceptibility at higher temperatures an electrically heated silica tube furnace was used. The variations in temperature near the pole pieces on account of the furnace were found not to affect the field strength, because the pull per gram observed for a

standard diamagnetic, at various temperatures was found to be unaffected. In order to see whether the substance in the tube had actually attained the temperature recorded by the thermometer in the electric furnace, a magnetic examination of manganese pyrophosphate, prepared from analytically pure manganese sulphate, was undertaken. The calculation of temperature was made by the aid of the Curie-Weiss law,

$$\chi_M = \frac{C_M}{T - \theta}$$

the value of $\theta = 23^\circ$, being known for this compound.

The observed and the calculated temperatures are recorded below. The agreement is excellent.

TABLE IV.

Reading	..	1.	2.	3	4.	5	
$\chi \times 10^6$...	102.8	95.79	89.50	77.93	68.63	
Temp. {	Obs ($^{\circ}\text{K}$)	...	300	324	348	404	461
	Calc ($^{\circ}\text{K}$)	...	—	323	348	403.8	460.8

The magnetic susceptibilities of the cobaltous oxides are recorded in Table V and the variation of χ values with temperatures in Table VI, each value represents the mean of at least three independent observations. The Bohr magneton number μ_B is calculated from the formula $\mu_B = 2.839 \sqrt{\chi_M(T - \theta)}$ where χ_M corresponding to the observed χ is calculated for one metallic atom per molecule and θ , the Curie point is determined by plotting the $(1/\chi_M - T)$ graph and reading off θ as the intercept on the T -axis. In the case of cobaltous oxide the variation of $1/\chi_M$ with T is not linear below $80^\circ - 90^\circ$ and the value of θ was calculated from χ values at higher temperatures.

TABLE V.

Susceptibility of cobaltous oxide at 23° .

Method of preparation.	Colour.	χ .	Method of preparation.	Colour.	χ .
I	Yellowish grey	68.14×10^{-6}	IV	Greyish black	Ferro magnetic
II	"	68.14	V	Brownish black	57.49
III	"	68.45	VI	Greyish black	61.238

TABLE VI.

*Variation of Magnetic susceptibility with temperature.*1. *Cobaltous oxide.*(i) Sample prepared by heating cobalt carbonate in *vacuo*.

Temp.	χ .	χ_M .	θ from graph.	C_M calc.	C_M mean.	μ_B .
293°K	68.14×10^{-6}	5109.0×10^{-6}		3.199		
341	66.07	4953.0		3.339		
361	65.00	4873.0	-330°K	3.383	3.387	5.225
393	62.07	4654.0		3.379		
457	57.22	4289.0		3.388		
492	55.04	4127.0		3.397		

(ii) Sample prepared by heating cobalt carbonate in carbon dioxide

296°K	68.74×10^{-6}	5153.0×10^{-6}		3.071		
324	68.21	5113.0		2.191		
348	66.89	5016.0		3.250		
355	66.13	4958.0		3.247		
			-300°K		3.243	5.113
375	64.28	4819.0		3.253		
398	62.12	4646.0		3.243		
465	56.28	4220.0		3.282		
495	54.28	4069.0		3.235		

(iii) Sample prepared by heating cobalt hydroxide in carbon dioxide

296°K	68.45×10^{-6}	5133.0×10^{-6}		3.120		
325	66.02	5099.0		3.248		
348	66.03	4950.0		3.267		
355	65.33	4898.0		3.267		
			-312°K		3.267	5.131
375	63.22	4740.0		3.256		
398	61.35	4599.0		3.266		
465	55.97	4196.0		3.260		
495	54.26	4068.0		3.283		

TABLE VI (contd.).

2. Cobaltous oxide.

(i) Prepared by ignition of cobalt nitrate.

Temp.	-X.	X _m .	θ from graph.	C _m calc.	C _m mean.	μ_E
293°K	30'73 $\times 10^{-6}$	2468'0 $\times 10^{-6}$		1'098		
314	29'47	2367'0		1'104		
340	27'81	2233'0		1'098		
			-152°K		1'101	2'979
395	25'03	2010'0		1'100		
454	22'58	1813'0		1'099		
505	20'82	1672'0		1'098		

(ii) Prepared by calcining cobalt oxalate.

293°K	30'63 $\times 10^{-6}$	2460'0 $\times 10^{-6}$		1'100		
301	30'00	2409'0		1'096		
313	29'39	2359'0		1'102		
			-154°K		1'102	2'981
338	27'93	2243'0		1'104		
393	25'42	2041'0		1'116		
457	22'51	1807'0		1'104		
503	20'63	1657'0		1'088		

(iii) Prepared by heating a mixture of cobalt and ammonium chlorides.

293°K	30'94 $\times 10^{-6}$	2484'0 $\times 10^{-6}$		1'108		
307	29'86	2397'0		1'104		
332	28'40	2280'0		1'106		
			-153°K		1'106	2'986
355	27'15	2180'0		1'108		
410	24'44	1963'0		1'104		
460	22'50	1807'0		1'108		
506	20'95	1683'0		1'109		

3. Cobaltic Oxide

(i) Sample prepared by heating cobalt nitrate at 184°.

293°K	28'63 $\times 10^{-6}$	2375'0 $\times 10^{-6}$		1'137		
319	27'01	2242'0		1'131		
341	26'05	2162'0		1'140		
			-186°K		1'136	3'026
393	23'66	1963'0		1'137		
457	21'27	1765'0		1'134		

(ii) Prepared by oxidising cobalt chloride with potassium chlorate.

296°K	28'98 $\times 10^{-6}$	2405'0 $\times 10^{-6}$		1'131		
323	27'46	2279'0		1'132		
			-174°K		1'132	3'021
349	25'93	2152'0		1'126		
397	23'95	1988'0		1'135		
461	21'51	1784'0		1'133		

DISCUSSION.

An examination of Tables V and VI shows that the samples of cobaltous oxide prepared by heating (i) cobalt carbonate in vacuum, (ii) cobalt carbonate in carbon dioxide, and (iii) cobaltous hydroxide in CO_2 , are all yellowish grey in colour and give a magnetic susceptibility value of $(68.45 \pm 0.30) \times 10^{-6}$ at 23° . It will be noticed that fairly constant values for χ are obtained in spite of the fact that the methods of preparation are different.

The cobaltous oxide, prepared by heating cobalt metal in a stream of nitric oxide at 150° (Table V, sample IV), is greyish black in colour and ferromagnetic; in oxide prepared by reduction of Co_2O_3 by NH_3 is brownish yellow, having a susceptibility value of 57.49×10^{-6} and the oxide (sample VI) prepared by the reduction of Co_3O_4 is greyish black and has a χ value of 61.238×10^{-6} .

The ferromagnetism of the oxide, prepared by heating cobalt metal in an atmosphere of NO , is attributable to the presence of some unreacted metal. This conclusion is supported by the analytical results shown in Table III which reveal the presence of free metal.

The low susceptibility value observed for cobaltous oxide, prepared by passing a current of ammonia over cobaltic oxide, may be due to (1) the presence of some higher oxide of cobalt or (2) more probably to a complex compound formed by the adsorption of ammonia on the oxide surface.

As regards the first possibility, the only higher oxide present, can be Co_3O_4 , since Co_2O_3 is not likely to exist at the temperature of the experiment. The calculated χ value of the sample on the assumption that it is a mixture of CoO and Co_3O_4 works out to 65.48×10^{-6} . The value actually obtained is 57.49×10^{-6} . It seems, therefore, that the low value of χ obtained for the product cannot be wholly accounted for by the formation of Co_3O_4 . The formation of some adsorption complex with ammonia is also suggested. Analytical results in fact did show the presence of ammonia in traces.

The sample VI (Table V) obtained by reduction of Co_3O_4 with carbon also gives a low χ value. Kalmuss (*loc. cit.*) has suggested that the oxide prepared in this manner is an allotropic modification of the ordinary cobaltous oxide but no evidence has been adduced to justify this assumption. The other possibility is that the difference in susceptibility may be due to the sample being a mixture or solid solution of different oxides; cobaltous and cobaltosic oxides are known to exist in solid solution. The presence of Co_3O_4 will bring down the χ value of the oxide.

The calculated χ value for the sample on the assumption that it is a solid solution of the two oxides comes to be 65.36×10^{-6} . The observed value is 61.26×10^{-6} and consequently magnetic evidence is against the mere formation of a simple solid solution of the two oxides. It is therefore suggested that this product is a complex of the type $\text{CoO} \cdot \text{NO}$ (*vide infra*).

The authors have studied the effect of temperature on the χ value of cobaltous oxide and the results are given in Table VI. The $(1/\chi_M, T)$ curves for the three samples of CoO show a discontinuity at $80^\circ\text{--}88^\circ$, indicating that a new phase makes its appearance at this temperature. The value of θ obtained by interpolation of the graphs from the susceptibility values beyond this temperature varied from 300° to 333°K .

The value of the Bohr magneton number, $\mu_B = 5.169 \pm 0.056$ is found to agree exceedingly well with the theoretical value for the cobaltous ion. The Co being in $4F_{9/2}$ state gives Bohr magneton number μ_B of 5.20 . If the orbital moment is fully quenched by a crystalline field, the spin moment alone is effective and the value of μ_B reduces to 3.87 . Since the experimental value is 5.169 ± 0.056 , it is clear that the cobalt ion in CoO is in the Co^{++} state and the orbital moment is quite free to operate. Hence the molecular formula, CoO for cobaltous oxide, very well explains the known data about it. At temperatures below 80° , the value of μ_B moves in the direction of 'spin only'.

Squire (*J. Chem. Phys.*, 1939, 7, 139) found that the paramagnetism of manganous oxide drops to nearly diamagnetism with decrease of temperature from 298° to 14°K and he expressed a similar view in explaining it.

Bhatnagar, King and collaborators (*loc. cit.*) observed a break in the χ - T curve for Cr_2O_3 at 65° and explained the anomaly in a similar manner.

Cobaltous and Cobaltic Oxides.

The cobaltous oxide shows a χ value of $(30.78 \pm 0.15) \times 10^{-6}$. The χ - T curve is smooth and the value of θ , obtained by interpolation, is -153 ± 1 . The Bohr magneton number μ_B is 2.982 ± 0.0035 . It is significant to note that in spite of the methods of preparation being different, the susceptibility value is constant for the compound.

The magnetic susceptibility of the two samples of Co_2O_3 has been determined. The values of χ for the two preparations of Co_2O_3 are 28.63×10^{-6} and 28.98×10^{-6} at 23° . The θ value found by interpolation on the χ - T curve was 186° and 174° and $\mu_B = 3.02$. Co is in $5D_4$ state. The theoretical value of the magnetic moment for trivalent cobalt ion lies between 4.9 and 5.48 . The experimental value, however, is much lower.

There is a great deal of uncertainty about the constitution of the oxide stated in literature to be Co_2O_3 . Mobius and Blanc (*loc.cit.*) doubt very much if cobaltic oxide can be produced by the dry methods. The alleged cobaltic oxide is considered to be a solid solution of oxygen in cobaltous oxide: cobaltous oxide adsorbs oxygen, forming the system $\text{Co}_3\text{O}_4.m\text{O}_2$ and though the analysis makes it appear as Co_2O_3 or even a higher oxide of cobalt, there is no change in the lattice structure of Co_3O_4 . Indeed Mobius has stated that all the methods described in literature for preparing cobaltic oxide really furnish solid solutions of the type $\text{Co}_3\text{O}_4.m\text{O}_2$.

It seems that in cobaltous and cobaltic oxides the arrangement of the Co atom is just the same as that in CoO with the difference that in these oxides the orbital moments are fully quenched due to the combination of CoO molecules themselves. Now if that were the only change then the μ_r value would have been 3.87. The experimental value for Co_2O_3 is 3.02 and for Co_3O_4 2.98.

The adsorption of oxygen by CoO results in the lowering of the χ value (*vide infra*). It can therefore be inferred that the observed low value of μ_r for these oxides is due to the formation of complexes $3\text{CoO}\cdot\text{O}$ and $2\text{CoO}\cdot\text{O}$ respectively. The molecules of cobaltous and cobaltic oxides do not appear to exist as Co_3O_4 and Co_2O_3 .

The Effect of Oxygen Adsorption on CoO.

For the study of oxygen adsorption by cobaltous oxide the following procedure was adopted. Oxygen was passed over the oxide at different temperatures and the effect on χ value was determined. The exposed product was evacuated at (i) room temperature and (ii) the temperature at which adsorption was carried out and χ values again determined. The results are tabulated below (Table VII).

From Table VII it will be seen that originally the samples had no oxygen adsorbed on them since the χ value did not change on evacuation at 23° and at 100° . The susceptibility of the oxide uniformly decreases with the adsorption of oxygen and this effect becomes more marked at higher temperatures. Up to 80° the oxide regains more or less, its original value but when oxygen is passed at higher temperatures the value is not regained on evacuation.

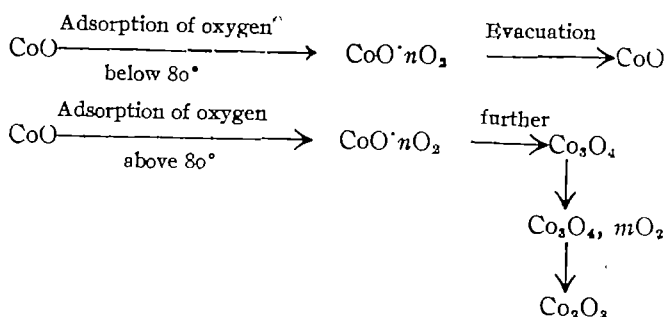
The colour of the oxide also shows corresponding changes. Cobaltous oxide is yellowish grey but after oxygen adsorption it changes to brownish grey. Below 80° the oxide regains its original colour on evacuation, whereas the oxide treated at higher temperature undergoes a permanent change. Oxygen is adsorbed by CoO and a more or less loose adsorption complex

TABLE VII.

Treatment	Susceptibility values of cobaltous oxide samples ($\chi \times 10^6$).			Colour.
	I	II	III	
1. Evacuated at				
(i) 23°	68.14	68.73	68.44	Yellowish grey
(ii) 100°	68.14	68.744	68.445	"
2. Oxygen passed at				
23° for 1 hr.	68.03	68.60	68.160	"
Evacuated at 23°	68.12	68.71	68.41	"
3. (i) Oxygen passed at 80° for 1 hr.	67.28	67.39	67.33	Brownish tinge
(ii) Evacuated at				
(a) 23°	68.07	68.60	68.39	Yellowish grey
(b) 80°	68.08	68.71	68.401	"
4. (i) Oxygen passed at 120-30° for 1 hr.	65.42	65.80	65.47	Brownish yellowish grey
(ii) Evacuated at				
(a) 23°	66.01	66.31	66.12	A little less brownish tinge
(b) 120-30°	67.60	67.82	67.66	
5. (i) Oxygen passed at 200° for 2 hr.	46.64	46.89	46.245	Brownish grey
(ii) Evacuated at				
(a) 23°	48.00	48.14	48.16	"
(b) 200°	48.93	49.09	49.103	"

is formed which breaks up on evacuation but at higher temperatures there is a radical change. It seems therefore that below 80°, CoO adsorbs oxygen forming a loose adsorption complex or solid solution of the type $\text{CoO} \cdot n\text{O}_2$ which at higher temperatures passes into Co_3O_4 , this Co_3O_4 can further adsorb oxygen forming $\text{Co}_3\text{O}_4 \cdot m\text{O}_2$. Now if the taking up of oxygen by CoO were purely a physical phenomenon then the susceptibility of the adsorption complex $\text{CoO} \cdot n\text{O}_2$ should increase because of the greater paramagnetism of oxygen (107.4×10^{-6}). The data given in Table VII, however, reveals that the susceptibility value of the complex has fallen. It appears therefore that the adsorption of oxygen by CoO is physicochemical in nature and the complex formed has low susceptibility value. The regaining of the original χ value after evacuation below 80° indicates that

the behaviour of $\text{CoO} \cdot n\text{O}_2$ complex is just like the palladium-hydrogen adsorption complex studied by Sveusson (*Ann. Physik*, 1933, 18, 299). At higher temperature the complex $\text{CoO} \cdot n\text{O}_2$ passes into relatively stable Co_3O_4 , this further adsorbs oxygen to form the complex $\text{Co}_3\text{O}_4 \cdot m\text{O}_2$ and finally cobaltic oxide. The changes that are involved on the adsorption of oxygen by CoO can be represented as follows.



Effect of Variation in Mode and Time of Heating on Cobaltous Oxide.

Cobaltous oxide was prepared by calcining cobaltous nitrate at about 800° - 900° in (i) electric furnace (*vide supra*) and (ii) blowpipe flame for different intervals of time. The samples of the oxide obtained were analysed for cobalt and the susceptibility values determined, the results obtained are given in Table VIII.

TABLE VIII.
Cobaltous oxide.

Mode of heating.	Time of heating.	Cobalt		Susceptibility values.
		Found.	Calc.	
Electric furnace	(a) 2 hrs.	73.34 %	73.43 %	30.52×10^{-6}
	(b) 3 hrs.	73.333	"	30.58
	(c) 4 hrs. and upwards	73.364	"	30.554
Blowpipe	(a) 1 hr.	73.403	"	31.52
	(b) 2 hrs.	73.65	"	36.90
	(c) 3 hrs.	73.87	"	37.63
	(d) 4 hrs. and upwards	74.849	"	Ferromagnetic variety was obtained

It will be seen from the results given in Table VIII that the samples prepared by heating cobalt nitrate in the electric furnace for different

intervals of time have the same χ values. The χ values for the second series of samples prepared in the blowpipe, however, shows a marked variation so much so that it was found possible to obtain finally a ferromagnetic variety. The change in the χ value in the latter case is due, no doubt to introduction of some soot particles from the blowpipe which reduced Co_3O_4 to CoO and finally to the metal itself. In order to test this view two sets of experiments were performed.

Some soot from the blowpipe was introduced into the electric furnace sample which was then heated for sometime in the electric furnace. This sample gave a χ value of 37.73×10^{-6} . On adding a further amount of soot and heating as before the χ -value obtained was 40.32×10^{-6} .

In another case cobalt nitrate was heated in a silica crucible with a lid, using a clear blow pipe flame for about 3 hours. Good care was taken that no soot particles had access to the oxide. The sample on analysis for cobalt gave 73.44% and showed a χ value of 31.46×10^{-6} . This value is higher than the values for pure Co_3O_4 (*vide supra*) so that the conclusion is irresistible that extreme care is necessary in order to avoid the formation of metal by reduction.

It is suggested that if due regard be paid to the purity of the oxides and if the distortions produced by interatomic forces are taken into consideration, magnetic measurements are capable of giving important evidence as to the structure of oxides, while even a slight impurity totally vitiates the conclusions.

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Received July 8, 1941.

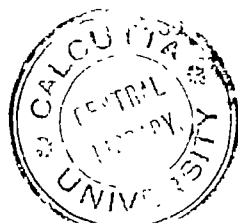
REVIEW

Principles and Practice of Chromatography BY ZECHMEISTER AND CHOLNOKY, TRANSLATED FROM THE ORIGINAL GERMAN BY A. L. BACHARACH AND F. A. ROBINSON. PUBLISHED BY CHAPMAN AND HALL, LONDON, 1941.

A comprehensive volume in English on the theory and practice of Chromatography with references of widely scattered literatures on the subject was a long-felt need. The English translation of the original German work and the publication of it under the above title will no doubt go far towards its removal. In the first decade of the current century Tswett, a Russian botanist, introduced chromatographic procedure in chemical analysis. He held that like the light radiations in the spectrum a solution mixture of different substances could be separated on an adsorbent column into its constituents, which can then be determined quantitatively and qualitatively. The theoretical basis of this assumption is that different substances have got different adsorption affinities and also different degrees of activity to the same adsorbent. So when a common solution of several substances is allowed to percolate through a column of suitable adsorbent, the individual components form well-defined layers in a descending order, corresponding with the diminution in their surface activities towards the adsorbent. This fundamental concept of Tswett and his method achieved far-reaching actuality at the moment when the classical enzyme researches of Willstätter and his school made it clear that surprisingly fine differences of structure can be demonstrated by systematically conducted adsorption and elution. In recent years in the hands of Karrer, as well as of Kuhn, Winsterstein and others, Tswett's method has proved to be of unique success for the study of vitamins, hormones, carotenoids and other natural pigments. Indeed, chromatographic technique is now at the beginning of a brilliant development and will soon extend to cover a varied field of research.

The book under review is divided into two parts. The first one deals with the fundamental principles of the method, its scope and the relation between chemical constitution and adsorption affinities of substances for the adsorbents. It also contains some details of actual procedure and particulars of apparatuses, adsorbents and solvents that are being widely used by different workers. In the second part experimental details of chromatographic separation and purification of many coloured and colourless substances such as chlorophyll, carotenoids, terpenes, sterols, vitamins, hormones, enzyme, etc. have been discussed. Ample suggestions on the selection of the best conditions for chromatographic analyses are one of the most commendable features of the book. References of works, mainly German, will be much helpfull to those interested in chromatographic technique.

S. R.





THE SEED FAT OF *BUCHANANIA LATIFOLIA**

BY N. N. GODBOLE, B. G. GUNDE AND P. D. SRIVASTAVA.

The component fatty acids of *Buchanania Latifolia* seed fat were found to be : palmitic 29%, stearic 8%, oleic 57% and linoleic 6% (by weight). It contains 4.8% of fully saturated glycerides. The glyceride structure of the fat follows the usual rule of "even distribution"

Buchanania latifolia, Roxb. (N.O. Anacardiaceae) (Indian name—Chironji), is a very common tree of the Indian forests. It bears in summer cherry like fruits, of which the upper thin skin and the seed enclosed in a hard round shell are edible. The seeds, light brown in colour, are very commonly used in confectionery, while the oil from the seeds is used as a substitute for almond oil for medicinal purposes. The seed, as well as the oil are recommended for cure of certain skin diseases by Indian physicians.

Of the seed fats belonging to this family (Anacardiaceae) only those mentioned below seem to have been analysed so far for their component fatty acid content.

(a) *Pistacia vera* (Dhingra and Hilditch, *J. Soc. Chem. Ind.*, 1931, 50, 97).

(b) *Antrocaryon Nannani* (Pieraerts and Ipatiev, *Mat. glasses*, 1927, 19, 7974).

(c) *Anacardium Occidentale* (Patel, Sudborough and Watson, *J. Ind. Inst. Sci.*, 1923, 6, 111).

From the present study, as well as from the analyses of the above fats it would be seen that in general, the predominating acids occurring in the seed fats of this family are palmitic, oleic and linoleic and in some cases stearic. Schaedler, ("Technologie der Fett und Öle," II, p. 668) and Bolton and Jesson (*Analyst*, 1915, 40, 3) have reported only the characteristic values of the oil from the seeds of *Buchanania latifolia* which along with the values of the present sample, are given in Table I.

It appears from Table I that although the three samples do not differ very much, the sample now analysed resembles more with the one reported by Schaedler.

* From the thesis submitted by P. D. Srivastava, for D.Sc. of the Benares Hindu University.

TABLE I.

Characteristics.	Schaedler.	Bolton & Jesson.	Present work.
Sp. gr. 30°/30°	—	—	0.9232
Melting point	32°	—	Liquid at room temp. (about 25°)
Solidification point	—	18°	—
Refractive index (40°)	—	—	1.4572
Acid value	15.4	51.8	32.7
Saponification value	193.6	198.7	193.2
Iodine value	57.3	55.0	62.4
R. M. value	0.33	—	—
Acetyl value	—	—	4.5
Unsaponifiables	—	2.15	1.07
Hehner value	—	—	93.1

EXPERIMENTAL.

The seeds (1 kg.), obtained from the local market, were cleaned, powdered and extracted with light petroleum (b. p. 40°-60°) in a Soxhlet apparatus. This gave 500 g. (50%) of a pale yellow fixed oil having a mild but agreeable aroma.

Another portion of 500 g. of the same powdered seeds was extracted with benzene, petroleum ether being not available. In this case the oil obtained (240 g., 48%) was of rather deeper colour and even after prolonged heating under reduced pressure, the smell of benzene could not be totally removed.

Both these samples of chironji fat, after dehydration and filtration, were separately examined for their general characteristics, given in Table II.

TABLE II.

	Extract.		Mixed sample.
	Petroleum ether	Benzene.	
Acid value	32.4	33.2	32.7
Saponification value	193.1	188.4	193.2
Iodine value	61.5	59.4	63.4

Since both the samples did not differ much (low sap. value of benzene extracted fat might be due to the presence of traces of the solvent) these were mixed for the present study. The characteristic values of the mixed sample are also given in Table II. In winter (room temp. 20-25°) a part

of the fat was found crystallising, suggesting the possibility of the presence of fully saturated or disaturated-mono-unsaturated glycerides. It was, therefore, considered worth while to study the glyceride structure of the fat along with the component fatty acids.

For the estimation of glycerides it was necessary to remove the free fatty acids from the fat. The fat (450 g.) was dissolved in four times its volume of ether and the solution treated twice with excess of 10% solution of potassium carbonate. The etheréal solution, washed free from alkali, on removing ether, gave 400 g. of neutral fat (S. E., 291'4; A. V., 0'0; I. V., 54'1). From the potassium carbonate washings 46 g. of fatty acids (S. E., 272'5; I. V., 59'7) were recovered. It would be seen from the characteristics of these recovered acids that these have a composition almost similar to that of component fatty acids of the neutral fat.

Component Acids.

The neutral oil (112 g.) was hydrolysed and the recovered fatty acids (103 g.) (S. E., 274'8; I. V., 61'8) were then separated into 'solid' (36'65%) and 'liquid' (63'35%) acids by means of the different solubility of their lead salts in alcohol (Hilditch *et al.*, *Biochem. J.*, 1929, **23**, 327). Each group of acids was then converted into the corresponding methyl esters which were fractionally distilled under vacuum (0'5-1'0 mm) from a Willstätter bulb. The fractionation data are given in Tables III and IV.

TABLE III.

Fractional distillation of methyl esters of the solid acids 'S'.

Fraction No.	Esters (S. E.=275'1; I. V.=4'2)			
	Wt.	B. p.	S. E.	I. V.
S ₁	3'23 g.	124°-38°	270 1	0 6
S ₂	3'07	138°	270'5	0'6
S ₃	4'01	138°-39°	274 0	2'3
S ₄	4'88	140°	274'5	2'5
S ₅	3'58	140°-43°	274'8	3 7
S ₆	3'71	143°-46°	275'8	5 5
S ₇	2'41	Falling	279'0	7'6
S ₈	4'79	Residue	299'8	13 5
	29'68			

TABLE IV.

Fractional distillation of methyl esters of the liquid acids 'L'.

Fraction No.	Esters (S. P.=297'5; I. V.=87'4)			
	Wt.	B. p.	S. E.	I. V.
L ₁	2'60 g.	115°-35°	289'5	74'10
L ₂	5'72	135°-50°	292'5	83'60
L ₃	3'66	150°-52°	294'7	89'80
L ₄	6'30	152°	295'0	90'00
L ₅	8'86	152°-56°	295'1	91'2
L ₆	8'32	156°-58°	295'2	93'6
L ₇	3'92	156°-58°	295'2	93'4
L ₈	2'67	Falling	295'1	93'20
L ₉	5'69	Residue	308'0	81'7
	47'74			

Examination of Individual Ester Fractions.

Fractions S₁, S₂.—Acids obtained from these fractions melted at 62°. On recrystallisation from alcohol (90%), the melting point rose to 62'5°. The presence of palmitic acid was thus confirmed.

Fraction S₈.—The residual fraction S₈ contained acids which, when freed from the unsaponifiable matter, had S. E., 279'4; I. V., 9'2. These acids when crystallised from acetone melted at 68°. This melting point remained unchanged on further crystallisations from acetone, thus indicating the absence of any acid higher than stearic.

Fraction L₉.—After removing the unsaponifiable matter the acids obtained from this fraction had S. E. 277'3 and I. V., 76'2.

Fractions L₈—L₉.—About 5 g. of the acids from these fractions were brominated in ethereal solution at 5° and allowed to stand at 0° for a long time, but no insoluble bromide separated. Linolenic acid is therefore absent. The residue from the above after removing ether was crystallised from light petroleum, when only a small amount of a crystalline product (m. p. 110°) separated indicating thereby the presence of ordinary seed fat linoleic acid.

A portion (about 3 g.) of the acids from fractions L₈—L₉ was oxidised in solution in dilute alkali at 0° by potassium permanganate, and the

products of oxidation extracted with light petroleum to remove any saturated acids. The products insoluble in light petroleum were separated by hot water into an insoluble and a soluble portion. The former yielded, on crystallisation from ethyl acetate, an acid m. p. 131° (mixed m. p. with 9:10-dihydroxystearic acid, 132°), while the residue obtained from the latter portion was too small for further examination. Presence of ordinary oleic acid was thus confirmed.

With the help of the above qualitative examination and the ester fractionation data given in Tables III and IV, the component acids of the fat of *B. Latifolia* are calculated (Table V).

TABLE V.

Acids.	Solid (36.65%).	Liquid (63.35%).	Fatty acids (ex-non-sap).		
			Total.	(%wt).	(%mol).
Myristic	—	0.14	0.14	0.1	0.2
Palmitic	26.54	2.19	28.73	28.9	30.9
Stearic	8.08	—	8.08	8.1	7.8
Oleic	1.90	55.15	57.05	57.4	55.7
Linoleic	—	5.44	5.44	5.5	5.4
Unsaponifiables	0.13	0.43	0.56	—	—

Component Glycerides.

The fully saturated glycerides (F. S. G.) of the fat were determined by the acetone-permanganate oxidation method. Oxidation was carried out in two batches A and B (53.1 g. and 75 g. respectively). The fat was dissolved in dry acetone (10 c.c. per g.) and oxidised with powdered potassium permanganate (4 g. per g. of fat). Batch A gave 2.48 g. of crude F. S. G. with A. V., 0.8; I. V., 1.3; whence % F. S. G. would be 4.4% (wt); while from batch B, 3.82 g. of crude F. S. G. with S. E., 276.2; A. V., 1.0; I. V., 1.2, were obtained, [whence % F. S. G., 4.8% (wt)]. It, therefore, follows that the fat contains 4.6% (wt) or 4.8% (mol.) of fully saturated glycerides. The acids, freed from the unsaponifiable matter, from the F. S. G. had S. E., 262.3.

From the above data and from those given in Table V for the whole fat, the distribution of the component fatty acids in the fully saturated and the mixed saturated-unsaturated parts of the fat is calculated as given in Table VI.

TABLE VI.

Balance sheet (molecular).

Acid.	Whole fat (100 mols)	F. S. G. (4.8 mols.)	Mixed part 95.2 mols (by diff.)	
Palmitic	31.1*	3.9	27.2	} 34.1
Stearic	7.6	0.9	6.9	
Oleic	55.7	—	55.7	} 61.1
Linoleic	5.4	—	5.4	

Association ratio (saturated : unsaturated) in the mixed part 0.56: 1

* This includes 0.2% of myristic also.

Thus the major component acids of *B. Latifolia* fat are palmitic and oleic, stearic and linoleic being only in small proportions. As may be expected from this composition and with due consideration to the well established 'rule of even distribution' (Hilditch *et al*, *loc. cit.*) the amount of fully saturated glycerides present is small. The component glycerides of the fully saturated part would be (calculated from its S. E.) tripalmitin (2.1 mols.) and steardipalmitin (2.7 mols.) For the mixed part two alternative combinations of glycerides are possible :

(a) Mono-saturated-di-unsaturated, (88.1 mols.) and disaturated-mono-unsaturated (7.1 mols) and (b) disaturated-mono-unsaturated (51.2 mols.) and triunsaturated (44.0 mols.) Of these the former combination (a) is more likely to be present according to the rule of even distribution. Since the amount of the fat was small, detailed glyceride structure estimation by crystallisation method could not be done. The present data are, however, sufficient to show the general distribution of the fatty acids in the glycerides of the fat.

STUDIES ON THE PHOTOCHEMICAL ACTIVITY OF MIXTURES OF VANADIC ACID AND TARTARIC ACID. PART II. PHOTOCATALYSIS BY COLLOIDAL MICELLE OBTAINED BY THE REDUCTION OF VANADIC ACID AND TARTARIC ACID: INDUCED OPTICAL ACTIVITY BY CIRCULARLY POLARISED LIGHT.

BY T. L. RAMA CHAR.

The influence of *d*- and *l*-circularly polarised light on the photocatalytic oxidation of tartaric acid by persulphate using as photocatalytic agent circularly dichroic micelles, obtained by the reduction of vanadic acid and *d*- or *l*-tartaric acid, has been studied, and differences obtained for the velocity of the reaction in *d*- and *l*-light. Dextro- and laevo-rotations have been induced by the action of circularly polarised light on the photo-oxidation of racemic acid by persulphate using as photocatalytic agent the colloidal micelle obtained by the reduction of vanadic acid and racemic acid.

Cotton (*J. chim. phys.*, 1909, 7, 87; *Trans. Faraday Soc.*, 1930, 26, 377) was the first to indicate that success in the field of 'Asymmetric Synthesis', might be achieved by making use of substances which exhibit circular dichroism. Modern theories of photochemical reactions postulate that the amount of photochemical transformation is proportional to the number of light quanta absorbed by the reacting molecules. If a racemic compound is illuminated by *d*-circularly polarised light, and the circular dichroism exhibited is such that the *d*-variety absorbs more of *d*-light than the *l*-variety, then it is to be expected that the rate of transformation of the *d*-variety will be faster than that of the *l*-variety. The result will be that, as photodecomposition proceeds in *d*-light, the inactive racemic mixture will develop increasing laevo-rotation. The essential conditions for success are, however, the following:

(i) The radiations used for photochemical transformation should correspond with the absorption band which is characteristic of the asymmetric electronic banding as indicated by Drude's equation for rotatory dispersion,

$$a = \sum \frac{k_m}{\lambda^2 - \lambda_{m_i}^2}$$

where a = observed rotation at wave-length λ , λ_m = wave-length corresponding to the characteristic frequency of vibration, and k_m = constant.

(ii) The substance should exhibit circular dichroism in the neighbourhood of the band head.

After Cotton's unsuccessful experiments (*loc. cit.*) several workers carried out photochemical reactions in circularly polarised light, as well as by passing plane-polarised light through a magnetic field parallel to its lines of force (Curie, *J. Physique*, 1894, **3**, 409); they did not get positive results. Kuhn and Braun (*Naturwiss.*, 1927, **17**, 227) were the first to demonstrate the asymmetric photodecomposition of an externally compensated compound. They observed a small rotation in the photolysis of alcoholic solutions of racemic-ethyl- α -bromopropionate in circularly polarised light. Kuhn and Knopf (*Naturwiss.*, 1930, **18**, 183; *Z. physikal. Chem.*, 1930, **B7**, 292) exposed to circularly polarised light hexane solutions of the racemic form of α -azidopropionic dimethylamide and obtained rotations of the order of a degree. Mitchell (*J. Chem. Soc.*, 1930, 1829) observed appreciable rotations on exposing the inactive humulene nitrosite to circularly polarised light. Karagunis and Drikos (*Z. physikal. Chem.*, 1934, **B26**, 428) obtained rotations of the order of 0.08° in the chlorination of the phenyl-biphenyl- α -naphthyl methyl radical in *d*- and *l*-light.

The well known experiments of Weigert (*Ann. Physik*, 1920, **36**, 681; *Naturwiss.*, 1928, **16**, 163) and Zocher and Copper (*Z. physikal. Chem.*, 1928, **132**, 303, 313) on the anisotropy of thin layers of silver halide, irradiated with polarised light, promise interesting developments. Bredig *et al* (*Biochem. Z.*, 1912, **46**, 7; 1932, **250**, 414) have demonstrated the parallelism between selective enzyme action and that of simple optically active catalysts.

In the present investigation, the influence of circularly polarised light on the photo-oxidation of tartaric acid by persulphate using photocatalytic colloidal systems, obtained by the reduction of vanadic acid and *d*-, *l*-, *dl*-, and racemic acids, has been studied.

Photocatalysis.

The red solution obtained by the addition of sodium metavanadate to *d*-, *l*- or racemic-tartaric acid does not exhibit circular dichroism in the visible region. On the other hand, if a mixture (at p_H less than 4) of *d*- or *l*-tartaric acid and sodium vanadate containing an excess of tartaric acid is exposed to light until the whole of the vanadium in the sol is reduced from the polyvanadic (V^5) to the polyvanadous (V^4) stage (Rama Char, *J. Indian Chem. Soc.*, 1941, **18**, 507) $V_2O_5 \rightarrow V_2O_4$, a violet or blue coloured colloidal solution is obtained which is both circularly dichroic and optically active,

This solution contains free tartaric acid and is quite stable up to p_H 3.3 for several days. The reduced sol obtained from racemic or *dl*-tartaric acid (mixture of *d*- and *l*- acids in equimolar proportions) is neither dichroic nor optically active.

It is well known that vanadyl compounds are powerful reducing agents. They also act as catalysts in some reactions, *e.g.*, reduction of chloric acid by hydrogen iodide, the catalytic action depending on an oscillation between the two oxides, V_2O_4 and V_2O_5 . The reduced vanadium micelle (*i.e.* reduced tartaric acid-vanadate colloidal micelle containing vanadium in the polyvanadous state) reduces hydrogen peroxide, potassium chlorate, persulphate, permanganate, bromine etc.; it is oxidised back in this process: V^3 (red or yellow) $\rightleftharpoons V^4$ (violet or blue). In all cases the rate of oxidation of V^4 increases with increasing p_H . At low p_H , however, the reduction of persulphate by the reduced micelle (which contains an excess of tartaric acid) is small in the dark, whereas the photochemical reaction proceeds rapidly in visible light, tartaric acid being oxidised in the process. In absence of vanadic acid, solutions of persulphate or their mixtures with tartaric acid do not undergo photochemical change in this region. The photoreduction of persulphate by tartaric acid has been found to be catalysed by the reduced vanadic acid-tartaric acid micelle.

EXPERIMENTAL.

Light from a mercury arc was rendered parallel by means of cylindrical lenses. Plane-polarised light was obtained by interposing in the path of the parallel beam a 'polaroid' supplied by the Polaroid Co. The plane polarised beam was then converted into two circularly polarised beams by means of a Fresnel Rhomb.

Measurement of Circular Dichroism in the Visible Region.

Bruhat (*Ann. physique*, 1915, 3, 232, 417; *Rev. Opt.*, 1929, 8, 413; *Bull. Soc. Chim.*, 1930, 47, 251) has developed a method for the determination of circular dichroism in the visible based on the principle that the axial relations of an elliptically polarised beam of light are changed on passing through a medium which has different absorption coefficients for *d*- and *l*-circularly polarised light. In the present investigation, the circular dichroism in the visible region was measured with an experimental arrangement which is a modification of Bruhat's apparatus. The complete arrangement as well as the method of measurement is described below.

Light from a point-o-lite 8000 c. p. Ediswan lamp after being rendered parallel by a suitable lens falls on the slit of a monochromator (Franz Schmidt and Haensch). It then passes through a polarimeter which consists of a half-shadow polariser and an analyser. A quarter-wave plate holder of the Bruhat's type was used; it rotates on a tubular bearing and carries a slide pierced with 3 holes, any one of which can be brought into register with the aperture of the bearing. Quarter-wave plates, which were correct for the wave-lengths used, were fitted into the two outer holes of the holder, and the arrangement, completed by the addition of a scale and a suitable rotating device, was mounted behind the polariser. A Baly's tube containing the solution under examination was placed between the quarter-wave plate and the analyser; it was provided with special end-plates having negligible birefringence.

The readings were taken as follows: a suitable half-shadow angle was chosen which was greater than the ellipticity to be measured. For a given value of this angle, the positions of the 'zero' of the analyser and the quarter-wave plate are practically the same for all the radiations. The Baly's tube containing the solution was then placed in position, the quarter-wave plate removed and the rotation reading taken in the usual way. The quarter-wave plate was then put back in position, and the equality of illumination was re-established thus: the quarter-wave plate was first turned in the sense which darkened the more illuminated side, the analyser was then turned in the same sense till the common illumination of both the sides was minimum, and the equality of the illumination was finally re-established by rotating the quarter-wave plate. There is no error in thus obtaining compensation for the rotation, if the quarter-wave plate is exact. The angle through which the quarter-wave plate was turned was finally read on the scale carrying it, and it gave the magnitude of the ellipticity of the solution. The sign of the ellipticity was determined by using Cotton's solutions.

The violet reduced vanadium micelle (*i.e.* colloidal micelle containing vanadium in the polyvanadous state, V^4) was obtained by exposing mixtures of the composition 0.08*M*-tartaric acid, 0.05*M*- $NaVO_3$ at p_H 2.8 to mercury arc for about 4 hours. The colloidal solution thus obtained was estimated for pentavalent vanadium (polyvanadic acid) iodometrically to ensure complete reduction. The circular dichroism (as ellipticity) and rotatory dispersion of the *d*- and *l*- reduced vanadium micelles (*i.e.* reduced sols obtained from mixtures of vanadate and *d*- and *l*- tartaric acid respectively) are given below. The rotation readings were correct to $\pm 0.01^\circ$ and the ellipticity readings correct to $\pm 0.02^\circ$.

TABLE I.

*d- Reduced micelle.*Conc. of reduced micelle (as vanadium) = 0.025*M*. $p_H = 3.2$.Temp. = 25°. l = length of solution.

Wave-length.	Length of soln.	Rotation.	Length of soln.	Ellipticity.
6700 Å	2 cm.	+0.24°	2 cm	-0.29°
6200	4	+0.41	4	-0.21
5780	4	+0.30	4	-0.10
5460	4	+0.19	4	-0.12
5200	3	+0.22	3	-0.07
4916	2	+0.16	4	-0.06

TABLE II.

l- Reduced micelle.

Conditions same as in Table I.

Wave-length.	Length of soln.	Rotation.	Length of soln.	Ellipticity.
6700 Å	2 cm.	-0.24°	2 cm.	+0.29°
6200	4	-0.42	4	+0.21
5780	4	-0.29	4	+0.09
5460	4	-0.19	4	+0.12
5209	3	-0.22	3	+0.07
4916	2	-0.16	4	+0.06

The results show that the *d*-reduced micelle has a positive rotation and negative ellipticity, whereas the *l*-reduced micelle has the reversed signs for rotation and ellipticity. The magnitude of the rotation as well as the ellipticity is the same for both the micelles in each wave-length. A negative value of ellipticity means that $\epsilon_l - \epsilon_d$ is negative (Mitcheli, "The Cotton Effect and Related Phenomena," 1933) where ϵ_l and ϵ_d are the molecular extinction coefficients in *l*- and *d*-light respectively, i.e., $\epsilon_d > \epsilon_l$ and the anisotropy factor g is negative. The *d*- and *l*-reduced micelles, therefore, have negative and positive values respectively for the anisotropy.

When mixtures of the reduced vanadium micelle and potassium persulphate were exposed to whole visible light (complete range using a 2% KNO_2 filter), it was observed that the initial violet colour did not change even in 8 hours. The mixtures were estimated for V^4 (polyvanadous acid) by microtitration with permanganate. Quick titrations gave satisfactory results in the presence of tartaric acid, and the titration was stopped when the pink colour due to permanganate persisted for 30 seconds. Titrations of the mixtures exposed to strong light for various periods from 4 to 8 hours showed that the concentration of V^4 had not changed. At the same time, iodometric titrations showed that the concentration of persulphate decreased on exposure of the mixtures to light. The titration values (corresponding to 1 c.c. of mixture) for a typical experiment are given below.

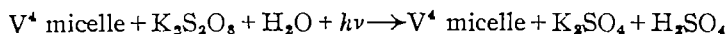
TABLE III.

Conc. of reduced vanadium = 0.025 *M*. Time of exposure = 4 hours.

Conc. of $\text{K}_2\text{S}_2\text{O}_8$ = 0.050 *M*.

	Estimation of V^4 (0.025 <i>N</i> - KMnO_4)	Estimation of $\text{K}_2\text{S}_2\text{O}_8$ (0.05 <i>N</i> -thiosulphate.)
Initial	2.0 c.c.	2.0 c.c.,
After exposure	2.0	1.3

These observations led to the conclusion that, since there is free tartaric acids in the reduced vanadium micelle, the latter acts as a photocatalyst in the oxidation of tartaric acid by persulphate :



V^5 micelle + tartaric acid + $h\nu \rightarrow \text{V}^4$ micelle + dihydroxytartaric acid, *i.e.* the V^4 (polyvanadous acid) micelle absorbs a quantum of light and reduces persulphate; it is itself oxidised to the V^5 (polyvanadic acid) stage and reduced back to V^4 by tartaric acid, and so on. The photocatalytic cycle, therefore, continues till one of the reactants, *i.e.*, tartaric acid or persulphate is completely transformed.

The photochemical reaction is very large compared with the dark reaction. Table IV gives the effect of the variation of the concentration of the reactants as well as the intensity of the absorbed radiation on the velocity of the photoreduction. dx/dt refers to the number of g. mols transformed per minute (with respect to persulphate), subtracting the dark reaction.

TABLE IV.

Radiation = whole visible Temp. = 25°. $k = \frac{dx/dt}{I_{\text{abs}} \times \text{conc. of } K_2S_2O_8}$

Conc. of <i>d</i> -reduced micelle.	Conc. of $K_2S_2O_8$.	I_{abs} .	dx/dt .	k
0.025 M	0.050 M	8650 ergs	13.3×10^{-5}	3.1×10^{-5}
"	0.025	"	6.5	3.0
"	0.013	"	3.3	3.1
0.013	0.050	5190	8.3	3.2
"	0.025	"	4.6	3.5
"	0.013	"	2.1	3.2
0.025	0.050	8650	13.3	3.1
0.013	"	5190	8.3	3.2
0.006	"	3460	5.4	3.1
0.025	"	8650	13.3	3.1
"	"	4325	6.7	3.1
"	"	2595	4.0	3.1
0.013	"	5190	8.3	3.2
"	"	2595	4.2	3.2

The above results show that the velocity of the reaction is proportional to the intensity of the light absorbed by the reduced micelle and the concentration of persulphate. For the same mixture, it is proportional to I_{abs} . Concordant values are obtained for the constant k . The velocity can, therefore, be expressed in the form

$$dx/dt = 3.1 \times 10^{-5} \times I_{\text{abs}} \times \text{conc. of } K_2S_2O_8.$$

Some reactions were carried out wherein *l*-, *dl*- and racemic-tartaric acids were used for obtaining the reduced vanadium micelle. The results given below show that there is no difference in the velocity of the reaction with these micelles.

TABLE V.

Other conditions same as in Table IV.

Conc. of reduced micelle.	Conc. of $K_2S_2O_8$.	I_{abs} for all micelles.	$\frac{dx/dt \times 10^5}{\text{Reduced micelle of}}$			
			<i>d</i> -H ₂ T.	<i>l</i> -H ₂ T.	<i>dl</i> -H ₂ T.	<i>rac</i> -H ₂ T.
0.025 M	0.050 M	8650 ergs	13.3	13.5	13.3	13.6
0.013	"	5190	8.3	8.3	8.3	8.5

Temperature Coefficient.—The temperature coefficient (35° - 25°) of this reaction is small, being of the order of 1.05

Reaction in Circularly Polarised Light.

Since the *d*- and *l*-reduced vanadium micelles exhibit circular dichroism in visible light, it might be expected that there will be a difference in the velocity of the reaction in *d*- and *l*-circularly polarised light. The experimental results conform to these expectations; they are given below. Permanganate titrations showed that the concentration of reduced vanadium (polyvanadous) did not change during the experiment.

TABLE VI.

Conc. of reduced micelle = 0.025 *M*. Temp. = 25° . $p_H = 3.65$.

Conc. of $K_2S_2O_8 = 0.050$ *M*. Radiation = whole visible.

$I_{abs} = 1384$ ergs in all cases.

Polarised light.	$\frac{dx}{dt} \times 10^8$ Reduced micelle of				(mean value).
	<i>d</i> -H ₂ T.	<i>l</i> -H ₂ T.	<i>dl</i> -H ₂ T.	<i>r</i> -H ₂ T.	
<i>d</i> -circular	2.71	1.87	2.30	2.30	0.25 to 0.36
<i>l</i> „	1.87	2.71	2.30	2.30	

TABLE VII.

Conc. of reduced micelle = 0.013 *M*. $p_H = 3.95$. Conc. of $K_2S_2O_8 = 0.050$ *M*.

$I_{abs} = 865$ ergs in all cases. Other conditions same as in Table VI.

Polarised light.	$\frac{dx}{dt} \times 10^8$ Reduced micelle of			
	<i>d</i> -H ₂ T.	<i>l</i> -H ₂ T.	<i>dl</i> -H ₂ T.	<i>r</i> H ₂ T.
<i>d</i> -circular	1.70	1.17	1.44	1.44
<i>l</i> „	1.17	1.70	1.44	1.44

The above results show that for the reaction with the *d*-reduced micelle, the velocity in *d*-light is greater than that in *l*-light, the reverse being the case for the *l*-reduced micelle. Also, there is no difference in the velocity in *d*- and *l*-light for the *dl*- or racemic-reduced micelles, the velocity being a mean of the velocities for the *d*- and *l*-micelles taken separately.

These results are in accordance with the dichroism exhibited by these micelles (Tables I and II). The *d*-reduced micelle has a negative anisotropy or $\epsilon_d > \epsilon_l$ i.e., larger fraction of the incident *d*-light is absorbed by the surface layers of the colloidal micelles. Only the radiation that is absorbed on the surface layer of the micelle is capable of bringing about photochemical

transformation, the radiation that penetrates the interior of the colloidal particle being ineffective for photo-reaction. The value of the quantum efficiency shows that about 30% of the total incident light is effective for chemical reaction. In the case of the *d*-reduced micelle, therefore, since $\epsilon_d > \epsilon_l$, the velocity in *d*-light is expected to be greater than that in *l*-light. The *l*-reduced micelle has a positive anisotropy, *i.e.*, $\epsilon_l > \epsilon_d$ and therefore, the velocity in *l*-light is expected to be greater than that in *d*-light. For the *dl*- or racemic-reduced micelles, on the other hand, $\epsilon_d = \epsilon_l$ and there should not be any difference in the velocity of reaction in *d*- and *l*-light. Tables I and II show that the ellipticity of the *d*- and *l*-reduced micelles has a high value (for the same length of solution) in the orange-red region, and that its value is quite large in the yellow, green and blue regions. Experiments performed showed that the photocatalytic reaction takes place in these regions.

Induced Optical Activity.

When racemic- or *dl*-reduced vanadium micelles are used, the velocity of the photoreduction of persulphate is the same in *d*- and *l*-circularly polarised light, and is a mean of the velocities with *d*- and *l*-reduced micelles. But the *d*- and *l*-reduced micelles are circularly dichroic. In view of the differential velocity and absorption of the *d*- and *l*-components for the same kind of light (*d*- or *l*-), therefore, it is to be expected that the exposure of mixtures of persulphate and racemic- or *dl*-reduced micelle to *d*- and *l*-light respectively, might result in the development of optical rotation of opposite sign; *i.e.*, *levo* and *dextro* respectively. The experimental results given in Table VIII conform to these expectations. The rotation was measured in a Winkel-Zeiss triple-field polarimeter which gave readings correct to $\pm 0.01^\circ$. Permanganate titrations showed that the concentration of the reduced vanadium (polyvanadous) did not change during the exposure.

TABLE VIII.

Length of solution (for rotation readings) = 2.6 cm. Wave-length (for rotation readings) = 5893 Å. Time of exposure = 8 hours.

Other conditions same as in Table VI.

Polarised light.	Observed rotation		Calc. rotation
	<i>dl</i> -H ₂ T micelle.	<i>r</i> -H ₂ T micelle	<i>dl</i> - or <i>r</i> -H ₂ T micelle.
<i>d</i> -circular	-0.06°	-0.06°	-0.06°
	+0.06	+0.06	+0.06

In the above table, the calculated value for the expected rotation is given by

$$\text{Rotation (calc.)} = \mp \frac{\text{Change in rotation on oxidation}}{\text{Change in titre on oxidation}} \times \frac{a-b}{a+b} \times c,$$

for *d*- and *l*- light respectively, where, the ratio (change in rotation/change in titre) is a constant, *a* and *b* are velocities of the photo-reduction (Table VI) with *d*-reduced micelle in *d*- and *l*-light, or with *l*-reduced micelle in *l*- and *d*- light, respectively (the final concentrations being the same as for *r*- or *dl*-reduced micelle), and *c*=change in titre actually observed immediately after the rotation was measured.

Mixtures of persulphate and *d*- or *l*-reduced micelle were exposed to light for different periods, the rotations were measured and the persulphate estimated. It was found that the ratio (change in rotation/change in titre) is a constant, equal to 4/3.

The experimental results given above show that when the racemic- or *dl*-mixture is exposed to *d*- light, it develops laevo-rotation, and when exposed to *l*- light, it develops dextro-rotation. There is good agreement between the observed and calculated values of the rotation.

The author wishes to express his thanks to Prof. J. C. Ghosh, for his kind interest and valuable suggestions during the investigation.

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Received June 3, 1941.

NORMAL ALUMINIUM CHROMATE.

BY PRODOSH CHANDRA RAYCHOUDHURY.

A method for the preparation of normal aluminium chromate has been reported and different properties of this substance thoroughly investigated.

From a study of the literature it appears that attempts by various workers to prepare normal aluminium chromate gave only basic chromates of variable composition such as $2\text{Al}_2\text{O}_3, \text{CrO}_3, 6\text{H}_2\text{O}$; $\text{Al}_2\text{O}_3, \text{CrO}_3, 7\text{H}_2\text{O}$, etc. all of which are insoluble in water. Comparatively recent literature on the subject also furnishes conflicting reports about the composition and constitution of this substance (*cf.* Calcagni, *Gazzetta*, 1925, 35, 396; Blanc, *Ann. Chim. phys.*, 1926, x, 6, 182; Charrion, *J. chim. phys.*, 1926, 23, 621; Briggs, *J. Chem. Soc.*, 1929, 242).

Thus it appears that normal aluminium chromate has probably not yet been known. While most of the above workers have been able to obtain an insoluble substance, none has yet obtained any aluminium chromate which is soluble in water. So it is thought that the investigation into the preparation and properties of normal aluminium chromate would be interesting.

EXPERIMENTAL.

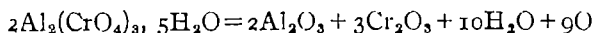
An excess of freshly prepared solid silver chromate with pure crystalline aluminium chloride were triturated in a mortar with the least possible quantity of ice-cold water. It was kept in a frigidaire for 3 days and the deep brown solution was decanted and filtered through quantitative filter paper twice. The solution was tested free from Ag^+ and Cl^- ions. It was evaporated in a vacuum desiccator containing concentrated sulphuric acid and kept in the frigidaire. A deep brown substance was obtained.

Both the brown solution and the solid were analysed. The chromate was determined iodometrically. A known weight of the substance was strongly heated till the weight of the mixture of the oxides was constant and also the weight of aluminium calculated from this. The ratio between $\text{Al}_2\text{O}_3 : \text{Cr}_2\text{O}_3$ was 1 : 3 in both the cases.

The solid was triturated with ice-cold glacial acetic acid several times. It was then dried in vacuum over concentrated sulphuric acid

and solid caustic potash in the frigidaire till a constant weight was obtained. The dry solid was then analysed as above. Results of analysis showed that $\text{Al}_2\text{O}_3 : \text{CrO}_3 : \text{H}_2\text{O}$ to be 1:3'004:5'005. This indicates that the formula of the compound is probably $\text{Al}_2\text{O}_3, 3\text{CrO}_3, 5\text{H}_2\text{O}$ i.e. $\text{Al}_2(\text{CrO}_4)_3, 5\text{H}_2\text{O}$.

Action of Heat.—By heating a known weight of the substance to a constant weight, a mixture of Al_2O_3 and Cr_2O_3 was obtained which contributed to the extent of 66'61% of the total weight of the substance. If, however, the composition of the substance be assumed as given above and if the reaction takes place according to the equation



the mixture of the oxides should amount to 67'01%.

Measurement of Molecular Conductivity.—The following figures show that the values for molecular conductivity of the substance at different dilutions (at 28°) are comparable to those of AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$ at 25°. This suggests that most probably the compound in solution electrolytically dissociates into five ions.

TABLE I.

Dilution (litres)	32	64	128	256	512	1024	2048	4096	8192
Mol. condy. (μ_v)	—	298'87	340'23	364'76	398'12	425'35	466'23	491'16	510 89
Mol. condy. of AlCl_3	—	—	342'00	371'00	393'00	413'00	—	—	—
Mol condy. of $\text{Al}_2(\text{SO}_4)_3$	158'01	—	219'04	—	301'01	—	425'05	514 06	—

Measurement of p_H .—A solution of the substance ($N/15$) was prepared by dissolving 1/90th of its formula weight per litre of solution. p_H values of this solution as well as those of an equivalent solution of chromic acid, AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$ and also of a $N/15$ solution of H_2SO_4 and CrCl_3 were determined at the room temperature with glass electrode. Results given below indicate the constitution of the substance to be similar to that of $\text{Al}_2(\text{SO}_4)_3$.

TABLE II.

Substance	$N/10\text{CrCl}_3$	$N/15\text{H}_2\text{SO}_4$	$N/15\text{H}_2\text{CrO}_4$	$N/15\text{AlCl}_3$	$N/15$	Substance	$N/15\text{Al}_2(\text{SO}_4)_3$
p_H	...	1'25	1'45	1'82	3'71	3'68	3'41

Degree of Hydrolysis.—It was calculated from the p_H value of the $N/15$ solution and was found to be $1'88 \times 10^{-2}$.

Chemical Properties.—The substance reacts acid to litmus. With NH_4OH and NaOH it produces a white gelatinous precipitate soluble in excess of NaOH . Concentrated AgNO_3 solution gave a red precipitate soluble in HNO_3 , while a dilute solution produced a black precipitate. Both BaCl_2 and lead acetate gave yellow precipitate soluble in HNO_3 in the case of barium salt. While K_2CrO_4 produced a brownish gelatinous precipitate soluble in acids, $\text{K}_2\text{Cr}_2\text{O}_7$ gave no precipitate. Mercuric chloride produced a white precipitate and H_2O_2 turned the solution deep violet which gradually turned brown.

These experiments evidently indicate that the compound formed is probably the normal aluminium chromate, $\text{Al}_2(\text{CrO}_4)_3, 5\text{H}_2\text{O}$.

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Received August 7, 1941.

PERIODATES OF TRIVALENT METALS.

BY PRODOSH CHANDRA RAYCHOUDHURY.

Reaction of trisodium paraperiodate on trivalent metallic salts has been studied and also the tetravalent lead periodate and manganese mesoperiodate.

Only few trivalent periodates are known. Eakle (*Z. Kryst.*, 1896, 16, 576) has cursorily mentioned a metaperiodate, $\text{Al}_2(\text{IO}_4)_3 \cdot 3\text{H}_2\text{O}$; Rammelsberg (*Pogg. Ann.*, 1838, 44, 559) prepared ferric mesoperiodate, $\text{FeIO}_3 \cdot 11\text{H}_2\text{O}$; Kimmins (*J. Chem. Soc.*, 1899, 55, 148) obtained tertiary ferric dimesoperiodate, FeH_2IO_3 and metaperiodate, $\text{Fe}(\text{IO}_4)_3$. Rammelsberg (*Ber.*, 1870, 3, 360) has also described a thallic periodate $3\text{Tl}_2\text{O}_3 \cdot \text{I}_2\text{O}_7 \cdot 30\text{H}_2\text{O}$.

The present investigation was undertaken with a view to studying the reaction of trisodium paraperiodate on some trivalent metallic salts and the properties of the compounds formed. Incidentally a tetravalent lead periodate and a manganese mesoperiodate were studied.

EXPERIMENTAL.

Bismuth Periodate.—Bismuth subnitrate was dissolved in concentrated nitric acid and trisodium paraperiodate, $\text{Na}_3\text{H}_2\text{IO}_6$, dissolved in dilute nitric acid, was added to it when a white precipitate was produced. It was allowed to settle and filtered, washed first with dilute nitric acid and finally with water till free from nitric acid. It was dried in a vacuum desiccator over concentrated sulphuric acid and solid caustic potash.

Bismuth periodate formed opaque crystals, insoluble in water and mineral acids. When strongly heated, it decomposes with evolution of iodine and formation of bismuth oxide.

Bismuth was estimated as Bi_2O_3 , and iodine volumetrically. (Found : Bi, 55.48; I, 24.3. Bi_2O_3 , $2\text{I}_2\text{O}_7$, $7\text{H}_2\text{O}$ requires Bi, 75.6; I, 22.5 per cent).

Aluminium Periodate.—Aluminium sulphate, dissolved in water was treated with a solution of trisodium paraperiodate in dilute nitric acid. No precipitate was formed even on concentrating the solution. So an aqueous solution of aluminium sulphate was added to a suspension of $\text{Na}_3\text{H}_2\text{IO}_6$ in water when a slight turbidity resulted. The mixture was placed over a water-bath, when after a short while, copious white precipitate was produced. It was filtered, washed with water till free from sulphate and dried in vacuum.

Aluminium periodate forms white crystals, soluble in nitric acid. On heating iodine was evolved and aluminium oxide was formed. (Found: Al, 11.06; I, 52.4. Al_2O_3 , $\text{I}_2\text{O}_7 \cdot \text{H}_2\text{O}$ or $\text{Al}_2\text{H}_2\text{I}_2\text{O}_{11}$ {Aluminium di-paraperiodate} requires Al, 11.11; I, 52.26 per cent).

Ferric Periodate.—To a nitric acid solution of trisodium paraperiodate a concentrated solution of ferric chloride was added. An immediate brown precipitate was produced. It was filtered, washed with water till free from acids, and dried in a vacuum desiccator.

The crystals are yellow and transparent, insoluble in cold and boiling water. They decompose on strongly heating. (Found: Fe, 15.9; I, 35.86. FeH_2IO_6 , $4\text{H}_2\text{O}$ requires Fe, 15.86; I, 36 per cent).

Thallic Periodate.—Thallic oxide, Tl_2O_3 , was digested with concentrated sulphuric acid and the solution was added to a nitric acid solution of $\text{Na}_2\text{H}_2\text{IO}_6$. After some time a yellowish brown precipitate was obtained. It was filtered, washed with dilute nitric acid and then with water till free of sulphate and dried in vacuum.

The yellowish brown crystals are insoluble in acids and decompose when strongly heated. Thallium was estimated as Tl_2O_3 . (Found: Tl, 60.5; I, 18.91. $2\text{Tl}_2\text{O}_3$, I_2O_7 , $3\text{H}_2\text{O}$ requires Tl, 61.26; I, 19.07 per cent).

Lead Periodate.—Lead tetra-acetate, was prepared according to the modified method of Oespar and Deasy (*J. Amer. Chem. Soc.*, 1939, **61**, 792). Freshly prepared pure and dry lead tetra-acetate was dissolved in the minimum quantity of pure glacial acetic acid. The solution was cooled in ice and diluted with twice its volume of ice-cooled 40% acetic acid and to it a solution of $\text{Na}_2\text{H}_2\text{IO}_6$, dissolved in 50% acetic acid, was added drop by drop with continuous stirring. At first there was no precipitate, but after a short while a brown precipitate was formed. It was washed with 50% acetic acid by decantation and filtered through a glass gooch, where it was again washed with glacial acetic acid, and dried in vacuum.

It forms brownish opaque powder. It is acted upon by boiling water and decomposes on strongly heating. Lead was estimated as sulphate after decomposition of the salt by strong sulphuric acid, and iodine volumetrically. (Found: Pb, 44.9; I, 26.75. 2PbO_2 , I_2O_7 , $5\text{H}_2\text{O}$ requires Pb, 44.32; I, 27.19 per cent).

Manganese Mesoperiodate.—Normal manganese periodate is unknown. Rammelsberg (*Pogg. Ann.*, 1868, **134**, 528) failed to prepare manganese periodate. He found that when alkali periodate was added to a solution of a Mn salt or periodic acid to MnCO_3 , a mixture of hydrated manganese dioxide and manganese iodate was obtained

A thin paste of an excess of Ag_2IO_6 was taken in a beaker, placed in a freezing mixture. An ice-cold solution of MnCl_2 was quickly poured into the beaker. Reaction took place with formation of silver chloride and a pink solution. The liquid was quickly filtered by a filter pump through a funnel surrounded by ice and the filtrate was collected in a beaker, which was placed in ice. The beaker was kept in a vacuum desiccator, containing concentrated sulphuric acid and solid caustic potash and kept in a refrigerator, the temperature of which was never above 15° . After two days beautiful pink crystals were formed. They were quickly filtered and dried in the vacuum desiccator kept in the refrigerator.

The crystals were stable below 15° , but above that temperature decomposed into black manganese hydroxide. Iodine was estimated volumetrically and manganese as Mn_2O_4 . [Found Mn, 28.70; I, 42.66. $\text{Mn}_2(\text{IO}_6)_2$ or $3\text{MnO}\cdot\text{I}_2\text{O}_7$ requires Mn, 28.5; I, 43.9 per cent].

Sincere thanks of the author are due to Prof. P. Rây for kindly permitting the author to work in his laboratory and for his kind interest in this work.

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Received August 13, 1941.

THE COLORIMETRIC (*p*-DIMETHYLAMINO BENZALDEHYDE-SULPHURIC ACID) METHOD FOR DETERMINING SMALL QUANTITIES OF ATROPINE.

By R. P. DAROGA.

A simple colorimetric method for the estimation of small quantities of atropine is recorded. Conditions for the optimum colour intensity have been obtained, and under the conditions laid down, the relationship between colour intensity and quantity of atropine is shown to be linear.

In the course of an investigation on the isolation and separation of the main constituents of *Datura* seeds, it became necessary to determine small quantities of atropine of the order of 0.1 to 0.5 mg. in small samples.

Existing methods, namely,

(i) Vitali's reaction ("L'Orosi," 1880; No. 8; *Arch. Pharm.*, 1881, *iii*, 18, 307).

(ii) Physiological test.

(iii) Gold chloride test.

(iv) Eder's micro tests with bromine water and bromo-potassium bromide ("Micro-sublimation in vacuo" Zurich, 1912).

(v) Gulielmo's odour test. (*Z. anal. Chem.*, 1863, 2, 404).

(vi) Gerrard's test. (*J. Pharm.*, 1884, 718).

being qualitative in nature, were valueless for quantitative assay.

Morin (*J. Pharm. chim.*, 1936, 128, 545) used Vitali's reaction (*loc. cit.*) for the determination of small amounts of atropine. For a quantity of 0.5 to 1.0 mg the colour is stated to be stable for 10 to 15 minutes and is intense violet. This method was found not sufficiently rapid for routine analysis.

Wasicky (*Z. anal. chem.*, 1915, 54, 393) noted the formation of a violet colour when atropine was warmed gently with *p*-dimethylamino-benzaldehyde-sulphuric acid reagent. According to Wasicky this is as delicate as the physiological test. A preliminary investigation showed that this reaction offered considerable promise.

An exhaustive examination of the reaction showed that the time, temperature and the concentration of the reagents influenced the colour intensity.

E X P E R I M E N T A L.

Procedure.—Wasicky's reagent was used for the preliminary experiments. 1 ml. of a standard solution of atropine in 10% sulphuric acid (*w/v*) (1.0 mg. of atropine per ml.) was introduced into each of the four thin glass dishes, containing a drop of the reagent. The dishes were heated on a water-bath for 30 minutes. After making the coloured solutions up to 50 ml. in graduated flasks, the colours were matched against permanent glass standards in a Lovibond-Schofield tintometer. The results are as follows:

TABLE I.

1.0 Mg. in each dish using 10 cm. cell for a period of 30 min.

Flask No.	Tintometer reading.			Flask No.	Tintometer reading.		
	Red.	Blue.	Scale reading.		Red.	Blue.	Scale reading.
1	0.9	0.1	+0.06	3	1.0	0.1	+0.06
2	0.8	0.1	+0.05	4	0.9	0.1	+0.06

It was found that violet colour appeared after 10 minutes' heating. The readings were taken immediately after dilution, as the colour subsequently faded.

Next, the time of heating was varied. The dishes were heated for one hour on a water-bath, and the colours matched as before.

TABLE II.

1.0 Mg. in each dish using 10 cm. cell for a period of 60 min.

Flask No.	Tintometer reading.			Flask No.	Tintometer reading.		
	Red.	Yellow.	Scale reading.		Red.	Yellow.	Scale reading.
1	4.1	0.8	+0.30	3	3.9	0.8	+0.24
2	4.0	0.9	+0.25	4	4.2	0.7	+0.31

The results indicate that the colour produced is not violet but orange, and in every case the tintometer reading (red) is higher than 30 minutes' heating experiments (Table I).

Effect of the Concentration of the Reagent.—A series of determinations were made using 0.1 ml. of the reagent. In previous experiments only one drop of the reagent was used.

The results in Table III indicate that the quantity of the reagent added also influences the colour intensity. Once again maximum red is obtained but the colour is orange. This colour is rather difficult to match, and is stable for ten minutes.

It was found that in order to obtain optimum violet colour, heating for 30 minutes was sufficient, and that the yellow colour was due to the strong reagent. The reagent was diluted 1:1 with water and 0.1 ml. of the dilute reagent was used in the following experiments.

The standard solution of atropine was introduced into each of the four dishes, and heated with 0.1 ml. of the dilute reagent for 30 minutes on a water-bath. The colours were matched as before after making up to 25 ml. in graduated flasks.

TABLE III.

1.0 Mg. in each dish using 10 cm. cell and 0.1 ml. of the reagent. Heating time=60 min.

Tintometer reading.				Tintometer reading.			
Time after dilution.	Red.	Yellow.	Scale reading.	Time after dilution	Red.	Yellow.	Scale reading.
Flask No. 1				Flask No. 2			
0 min.	7.1	3.2	+0.36	5 min.	7.2	3.1	+0.35
5	7.1	3.2	+0.36	25	6.4	3.0	+0.35
10	7.0	3.0	+0.35	30	6.2	2.9	+0.34
15	6.8	2.9	+0.34	40	6.1	2.8	+0.35
Flask No. 3				Flask No. 4			
5 min.	7.1	3.0	+0.35	5 min.	7.1	3.1	+0.35
15	6.7	2.9	+0.34	30	6.1	2.8	+0.34
30	6.1	2.8	+0.35	45	5.9	2.7	+0.33
40	6.0	2.9	+0.34	50	5.6	2.6	+0.33

TABLE IV.

Using 2 cm. cell and 0.1 ml. of the dilute reagent. Heating time=30 min. The colour when undiluted is stable, but slowly fades when diluted with water.

Tintometer reading.				Tintometer reading.			
Atropine.	Red.	Blue.	Scale reading.	Atropine.	Red.	Blue.	Scale reading.
0.55 mg.	3.3	0.2	+0.10	1.40	8.3	0.5	+0.35
0.65	3.9	0.2	+0.15	1.45	8.7	0.5	+0.40
0.95	5.7	0.3	+0.23	1.65	9.9	0.6	+0.45
1.35	8.1	0.5	+0.34				

The results (Table IV) obtained with this dilute reagent are of importance as the colour produced is violet and is suitable for colorimetric work.

The method as finally adopted.—The reagents used were :

(i) *p*-Dimethylaminobenzaldehyde-sulphuric acid.—2.0 G. of *p*-dimethylaminobenzaldehyde, dissolved in 10 ml. of concentrated sulphuric acid. This yellowish brown solution keeps for about four weeks, if stored in dark.

(ii) *Dilute reagent.*—The reagent (i) is diluted 1:1 with water before use. This reagent should be prepared fresh every day.

(iii) Standard solution of atropine in sulphuric acid.

0.1 Ml. of the reagent was added to the glass dish (10 ml. capacity) containing atropine. The glass dish was heated for 30 to 40 minutes on a water-bath. The solution was poured into a 25 ml. graduated flask, and diluted to the mark with water. The colour was immediately matched against permanent glass standards in the tintometer.

In general, colours of low intensity (0.1 to 1.0 mg. of atropine) were fully developed in 30 minutes whilst deeper colours (more than 1 mg. of atropine) required 40 minutes.

A number of determinations (Table V) was made, using the above method and the standard solution of atropine:

TABLE V.

Using the Lovibond-Schofield tintometer, cell = (2.0 cm.)

Atropine.	Red.	Blue	Scale reading. (+)	Total visual density.	Brightness.	Dominant hue wave-length mg. (Centre B).	Saturation L. P. D. (Centre B).
0.1 mg.	0.7	—	0.05	0.075	84.14%	509.0 mg.	3.5
0.2	1.2	0.1	0.06	0.13	74.13	508.5	7.0
0.3	1.8	0.1	0.07	0.17	67.61	505.0	10.0
0.4	2.5	0.2	0.10	0.215	60.95	504.0	14.0
0.5	3.1	0.2	0.10	0.26	54.95	503.0	17.5
0.6	3.6	0.2	0.15	0.32	47.86	503.0	21.0
0.7	4.2	0.3	0.20	0.385	42.17	502.5	25.0
0.8	4.9	0.3	0.20	0.425	37.58	502.5	28.0
0.9	5.5	0.3	0.23	0.50	31.62	502.2	31.5
1.0	6.0	0.3	0.24	0.54	28.84	502.0	35.0
1.1	6.7	0.4	0.25	0.60	25.12	502.0	38.0
1.2	7.2	0.4	0.30	0.65	22.39	501.5	41.5
1.3	7.8	0.5	0.34	0.72	19.05	501.4	45.0
1.4	8.4	0.5	0.35	0.76	17.38	501.0	49.0
1.5	9.0	0.5	0.40	0.82	15.14	501.0	52.0
1.6	9.7	0.5	0.40	0.85	14.13	500.2	55.1
1.7	10.3	0.6	0.45	0.91	12.3	500.0	59.0

The standard working curve for the determination of atropine illustrates the linear relation between colour intensity and concentration of atropine.

Analyses of the colour saturation and of the brightness were also made. There is a regular rate of increase of the colour saturation with the quantity of atropine. The transmission of light decreases fairly regularly as the quantity of atropine increases to 1.5 mg., and then becomes fairly constant.

In order to eliminate any possibility of error from the reagents, a second quantity was prepared, and a series of determinations made with atropine as before. The results (Table VI) agreed with those obtained with the first quantity of reagent.

TABLE VI.

Using the second stock of reagents; cell = 2 cm.

Atropine.	Tintometer reading.			Atropine.	Tintometer reading.		
	Red	Blue	Scale reading.		Red	Blue	Scale reading
0.50 mg.	3.1	0.2	+0.10	1.00	6.1	0.3	+0.24
0.65	3.8	0.2	0.15	1.35	8.1	0.5	0.34
0.70	4.1	0.3	0.20	1.45	8.7	0.5	0.40
0.95	5.6	0.3	0.23				

Evaporation of Atropine in Sulphuric Acid Solution.

A solution of atropine in an excess of dilute sulphuric acid can be evaporated down to 0.5-10 ml. approximately without loss. This was tested by introducing equal quantities of atropine into separate dishes containing 1 ml. of 10% sulphuric acid; then 10 ml. of water were added and the solution was evaporated down to 1 ml. by heating on a water-bath. The atropine in each dish was then determined, and the differences were within the experimental error.

Analytical Data.—The results obtained on known concentration of atropine, ranging between 0.1 mg. to 1.0 mg., using the above mentioned method are given in Table VII.

TABLE VII.

Recovery of known amounts of atropine.

Atropine in solution.	Atropine found from the standard curve	Recovery	Difference
0.100	0.095	95.0	- 5.0
0.100	0.090	90.0	- 10.0
0.500	0.475	95.0	- 5.0
0.500	0.500	100.0	0
1.00	1.00	100.0	0
1.00	0.975	97.5	- 2.5

They show good recovery of amounts of atropine ranging between 1.0 to 0.1 mg. With smaller amounts, viz. 0.1 mg., the recovery was about 10% lower than the theoretical yield.

The above method has been employed most advantageously for making numerous routine estimations of atropine. The method is being extended to determine small quantities of scopolamine and hyoscyamine.

The author wishes to express his thanks to Mr. A. A. Eldridge, F. I. C., for his kind interest during the work.

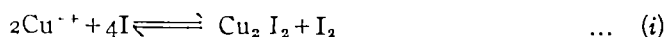
FOOD AND DRUGS DEPARTMENT,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON.

Received July 3, 1941.

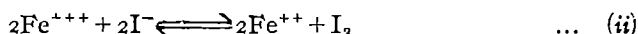
ESTIMATION OF COPPER IN PRESENCE OF IRON

By P. L. KAPUR AND BADAR-UD-DIN.

For the analysis of copper ores containing iron, it was required to devise a convenient and quick method for the estimation of copper when potassium or ammonium fluorides were not available. Cupric salts are usually determined iodometrically after precipitating Cu_2I_2 according to equation



Other radicals usually associated with copper ores such as iron arsenic and antimony interfere with the iodometric estimation of copper. Ferric iron is reduced by iodide,



but by addition of excess of potassium or ammonium fluoride, the ferric iron is converted into complex $(\text{FeF}_6)^{-}$ --- which yields so small concentration of ferric ions in the solution that it has no oxidising action upon the iodide and thus it enables a quick quantitative estimation of copper in presence of iron (Fraser, *J. Soc. Chem. Ind.*, 1915, **34** 462). If iron were present in a copper solution in the ferrous state then according to equation (ii) it would not react with KI, but as the reaction is reversible, part of it would be oxidised by the iodine liberated by copper ions according to equation (i). In presence of excess of potassium iodide, however, as the free iodine liberated by copper is removed by thiosulphate, any ferric ion formed would react with excess of potassium iodide present and would liberate that amount of iodine which was used before in the process of oxidation of Fe^{++} to Fe^{+++} . At the end the amount of iodine liberated by copper ions would be determined quantitatively. As the reaction (ii) is reversible so it will take time. Based on these considerations, following experiments were carried out and then a method to estimate copper in the presence of iron was evolved.

Iron and arsenic, in consequence of the oxidising medium usually employed to bring the copper ore into solution, would be present in solution in tri- and quinquivalent states respectively. Therefore sets of mixtures containing varying amounts of copper sulphate, ferric chloride and sodium arsenate were prepared. The solutions were reduced by zinc amalgam and sulphuric acid (Clowes and Coleman, "Quantitative Analysis" 14th edition 193, 1688). When reduction was complete the free acid in the solution was, neutralised with sodium carbonate and then acetic acid and

potassium iodide solutions were added to each of the solutions to be titrated. Iodine liberated was titrated against standard sodium thiosulphate solution using starch as indicator.

TABLE I.

A = 25% Acetic acid solution. B = 20% Potassium iodide solution.

Time taken for titration = 8-9 min.

No.	Vol of 2% CuSO ₄ , 5H ₂ O soln.	Vol. of 2% FeCl ₃ soln	Vol of 2% Na arsenate soln.	3.5 c.c A + 20 c.c B Room temp.	Vol. of N/10 thio Calc.	Found.
1	20 c.c	5 c.c.	5 c.c	30 c.c. H ₂ O	16.06 c.c.	16.06 c.c.
2	20	10	10	20	„	16.06
3	20	15	15	10	„	16.08
4	20	20	20	0	„	16.08
5	0	20	20	20	0	0.0

Thus it is clear from Table I that by this method copper can be estimated accurately iodometrically in the presence of other ions such as Fe⁺⁺⁺ and As⁺⁺⁺⁺ which ordinarily interfere in this estimation.

Copper content of four samples of copper ores was then determined by the reduction method outlined above and the results were further checked by the fluoride method. It was found (Table II) that the results obtained were in excellent agreement.

TABLE II.

Amount of ore taken.	Copper found by		Error
	Reduction method	Fluoride method.	
0.5 g.	20.36%	20.36%	0.0%
1.0	20.33	20.40	-0.7
1.5	20.46	20.38	+0.08
2.0	20.43	20.43	+0.0

ESTIMATION OF IODINE IN PERIODATES.

BY R. K. BAHL, SURJIT SINGH AND NARINDRA K. BALI.

A direct method for the estimation of iodine in the periodates, which give up the whole of iodine on heating, has been described. The results obtained by the new method have been compared with those obtained by Kimmin's method as modified by Partington and Bahl.

The estimation of iodine in periodates is carried out by the usual iodometric methods with slight modifications (Partington and Bahl, *J. Chem. Soc.*, 1934, 1087; Bahl and Singh, *J. Indian Chem. Soc.*, 1939, **16**, 269). Most of the periodates liberate the whole of their iodine content on strong heating and in such cases it has been found to be more convenient and accurate to determine its value directly.

P R O C E D U R E.

A preliminary experiment was performed by heating a small quantity of the periodate in a hard glass test tube till the whole of iodine was given out. The absence of any violet vapours of iodine even on the addition of a little concentrated sulphuric acid to the residue ensures complete evolution of iodine on heating.

The weighed salt (0.1 to 0.2 g.) was taken into a hard glass test tube, the open end of which was fused with a tube provided with two small bulbs. This in turn was connected to a bubbler containing a concentrated solution of potassium iodide. The tube with the bulbs was kept cool by covering it with a cotton pad soaked in cold water. The periodate lying in the end of the tube was strongly heated to ensure complete decomposition. It was disconnected from the bubbler and the iodine condensed in the cooler parts of the tube was washed down in a conical flask with a solution of potassium iodide. The dissolved iodine was titrated against a standard solution of sodium thiosulphate.

The table below shows the comparative values of iodine estimated by (a) Kimmin's method as modified by Partington and Bahl and (b) the direct method.

TABLE I.

Salts.	Sample	Iodine by (a).	Iodine by Calc value. (b)	
Cerium mesoperiodate tetra- hydrate, $\text{CeIO}_5 \cdot 4\text{H}_2\text{O}$	1	30.41%	30.26%	30.20%
	2	29.82	30.10	
Yttrium diorthoperiodate with 11 molecules of water, $\text{Y}_4\text{I}_2\text{O}_{13} \cdot 11\text{H}_2\text{O}$	1	25.40	25.27'	25.03
	2	25.20	25.23	
Yttrium mesoperiodate tetrahydrate, $\text{YIO}_5 \cdot 4\text{H}_2\text{O}$	1	33.50	33.49	33.54
	2	33.20	33.38	
Quaternary cupric paraperiodate monohydrate, $\text{Cu}_4\text{I}_2\text{O}_{11} \cdot \text{H}_2\text{O}$.	1	36.20	36.03	36.17
	2	36.51	36.41	
Cupric paraperiodate heptahydrate, $\text{Cu}_6(\text{IO}_6)_2 \cdot 7\text{H}_2\text{O}$	1	29.10	28.99	28.45
	2	29.12	29.04	
Cupric paraperiodate pentahydrate $\text{Cu}_6 \cdot \text{IO}_6)_2 \cdot 5\text{H}_2\text{O}$	1	29.45	29.71	29.75

DEPARTMENT OF CHEMISTRY,
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Received May 17, 1941.

A NOTE ON THE NEW FORMULA FOR CHAKSINE.

By S. SIDDIQUI AND Z. AHMAD.

In a recent paper by Kapur, Gaiind, Narang and Ray (*J. Indian Chem. Soc.*, 1940, 17, 281) a new formula $C_{11}H_{21}O_3N_3$ has been given to chaksine as against $C_{12}H_{21}O_2N_3$ tentatively assigned by us to the two isomeric bases chaksine and δ ochaksine, isolated as bicarbonate and carbonate respectively, from the seeds of *Cassia absus*, Linn. (*Proc. Indian Acad. Sci.*, 1935, 2A, 421). Ray *et al* state that they undertook this work, as the iodine content of the iodide noted by us was much too low,* and we had moreover relied on the analysis of chaksine bicarbonate "which was supposed to have the composition $C_{12}H_{20}ON_3 \cdot HCO_3, \frac{1}{2}H_2O$." They further state: "it was dehydrated by heating at 100° and the anhydrous substance analysed. There is grave objection to accept the loss in *vacuo* at 100° to be due to the loss of $\frac{1}{2}H_2O$. It is quite well known that the bicarbonates of organic bases, like those of an alkali metal, lose carbon dioxide on heating as indeed has been found to be the case by us."

It would appear from the above reference that the formula for the chaksine bicarbonate, $C_{12}H_{20}ON_3 \cdot HCO_3, \frac{1}{2}H_2O$, was derived by us only on the basis of an analysis of the anhydrous substance. This, however, is contrary to the facts. As would be seen from a reference to the original paper, the C, H and N values of the air-dried bicarbonate as well as of the anhydrous product were determined. Moreover, the loss of weight on drying at 100° in *vacuo* to constant weight was recorded and found to correspond to the required $\frac{1}{2}H_2O$. As regards the general behaviour of the carbonates or bicarbonates of the bases towards heat, pointed out by Ray *et al*, it would be well to recognise the large range of stability of the carbonates of organic bases, which principally varies with the strength of the basic radical but may also be due to other indeterminable factors. There are carbonates which decompose on heating in low boiling organic solvents while others are stable well above 200° . A parallel to the heat resistance of carbonates is the stability of certain hydrates. Generally speaking water of crystallisation is removed at 100° in *vacuo* but organic compounds are known which are completely dehydrated only at temperatures approaching 200° .

* Ray and collaborators' reference to our iodine value as 39.4 is apparently a misprint. The iodine content noted by us was 34.9 as against 36.39% calculated. This discrepancy in the iodine value of a quaternary iodide, dried at 100° in *vacuo*, had its obvious explanation.

However, considering the grounds on which Ray and co-workers undertook their work on chaksine, it would have been rational to expect an actual repetition of our work. This has been inexplicably avoided. Neither the carbonate nor the chloroplatinate have been analysed and the iodine content of the iodide has not been checked. On the contrary they have supported their C, H, and N values of the iodide with the iodine content noted by us. In this connection it is also striking that they have given the analytical data for C, H and N of the chloride and bromide but have avoided any reference to halogen values of these salts. As to the analytical data of the salts on which Ray *et al* have based their new formula for chaksine, it has further got to be noted that, except for the sulphate which melts at 317° and is highly incombustible, none of the other salts are noted by them to have been dried in *vacuo* to constant weight before analysis. Neglect of careful dehydration of the salts may have been partly responsible for their low carbon values.

In regard to the melting point of the iodide Ray and co-workers note 180° after drying in high *vacuo* at 100° , as against 168° (decomp.) recorded by us after drying at ordinary temperature in *vacuo*. A parallel observation of the melting points after drying under the same conditions would have been desirable, and it is surprising that they make no reference to it, as a quantity of the iodide was actually sent by one of us (S. S.) to the senior author at his own request.

In conclusion, it is obvious that the analysis of carbonates is not the best method of arriving at the formula of a base. As, however, the analysis of the pure base was excluded owing to the avidity with which chaksine and isochaksine absorb carbon dioxide from the atmosphere, and the undependability of carbon values in highly incombustible salts of alkaloids is a fact of common experience, a complete analysis of the chloroplatinate along with that of the carbonate, before and after drying at 100° , had to be admitted by us as a fair basis for a working molecular formula of chaksine and its isomer. Systematic investigation of the constitution of the two bases may eventually establish this formula or necessitate slight alterations. Work with this object is being carried out by us and the results will be communicated in due course.

BOARD OF SCIENTIFIC AND INDUSTRIAL
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Received September 11, 1941.

A NOTE ON THE SEPARATION OF SILICON AND TIN IN TIN-SILICA MIXTURE, WELDING BRASSES AND SILICON BRASSES BY ALKALI SULPHATE.

BY D. P. CHATTERJEE.

Both SiO_2 and SnO_2 are susceptible to be reacted by HF and NH_4I and thus incapable of being separated by HF and NH_4I . When a mixture of SiO_2 and SnO_2 is heated with HF a mixture of SnF_4 (b. p. 705°) and SiF_4 (gas) is obtained and when heated with NH_4I , a mixture of SnI_4 (341° sublimes) and SiI_4 (b. p. 290°) is obtained, but when the mixture of SiO_2 and SnO_2 is heated with HNO_3 and HCl , baked and diluted with HCl and water. H_4SiO_4 precipitates out and Sn remains in the solution, which is treated with a strong solution (15%) of Na_2SO_4 when Sn precipitates out which on ignition yields pure SnO_2 . A mixture of pure tin (Penang) and silica (obtained from pure Norwegian metal) was obtained in solution by aqua regia, baked with HCl , finally diluted with HCl and water when H_4SiO_4 which precipitates out is filtered, washed, ignited and weighed as SiO_2 , which weight is further checked by volatilising the SiO_2 with HF . Filtrate is treated with 15% Na_2SO_4 solution, when the precipitated Sn is filtered, ignited and weighed as SnO_2 , weight of SnO_2 being checked by volatilising the same with NH_4I . Welding brasses and silicon brasses contain both silicon and tin; both Sn and Si have been very successfully estimated by the above process. Presence of silicon increases the fluidity and tin the malleability in welding silicon brasses.

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Received July 25, 1941.



STUDIES ON THE PHOTOCHEMICAL ACTIVITY OF MIX-
TURES OF VANADIC ACID AND TARTARIC ACID. PART III.
INDUCED CIRCULAR DICHROISM IN VANADIC ACID SOL.
PHOTOREDUCTION OF DICHROIC SOL BY TARTARIC
ACID IN CIRCULARLY POLARISED LIGHT.

By T. L. RAMA CHAR.

Vanadic acid sol exhibits circular dichroism in the visible region on exposure to *d*- and *l*-circularly polarised light. The photoreduction of the dichroic sol by tartaric acid has been studied and differences have been obtained for the velocity of the reaction in *d*- and *l*-light.

Vanadic acid sol exhibits the phenomena of streaming anisotropy (Freundlich *et al*, *Köll. Chem.-Beih.*, 1915, 7, 195; *Z. physikal. Chem.*, 1924, 114, 161). The experiments of Weigert (*Naturwiss.*, 1928, 16, 163; *Z. physikal. Chem.*, 1929, B3, 377, 389; 1929, B4, 83) and Zocher and Coper (*Z. physikal. Chem.*, 1928, 132, 303, 313) on silver halide layers show that polarised light exerts an orienting influence on thin films, causing a transition from the isotropic to the anisotropic state. Ghosh *et al* (*J. Indian Chem. Soc.*, 1937, 14, 495, 617; *Kolloid Z.*, 1929, 86, 372) have shown that sols of vanadic acid, tungstic acid, chromic tungstate and ceric borate exhibit circular dichroism in ultraviolet, when they are exposed to *d*- and *l*-circularly polarised light, the anisotropy factor being negative and positive respectively. They have also found that, in photochemical reactions wherein these sols act as sensitisers or as oxidants, *l*-circularly polarised light gives a higher value for the reaction velocity than *d*-light. In a previous paper, the author has shown that, in the photocatalytic oxidation of tartaric acid by persulphate using circularly dichroic micelles obtained by the reduction of vanadic acid and *d*- or *l*-tartaric acid as catalyst; differences are obtained for the velocity of the reaction in *d*- and *l*-circularly polarised light (Rama Char, *J. Indian Chem. Soc.*, 1941, 18, 563).

In the present investigation, circular dichroism has been induced in vanadic acid sol by exposure to *d*- and *l*-light. The influence of *d*- and *l*-light on the photoreduction of the dichroic sol has been studied.

Induced Dichroism.

Vanadic acid sol was prepared by the action of acetic acid on sodium metavanadate; the colour of the sol was between red and orange. The

p_H of the sol was measured electrometrically by the glass electrode. Such a sol has no circular dichroism in the visible nor does it develop any on keeping in the dark for five hours. But on exposure of the freshly prepared sol to *d*- and *l*- circularly polarised visible light, it develops circular dichroism. The ellipticity measurements were made with the arrangement described in the Part II of this series (*loc. cit.*) The experimental results are given below. The ellipticity readings were correct to $\pm 0.02^\circ$.

TABLE I.

Conc. of vanadic acid sol (as V^5) = $0.10M$. Radiation = whole visible.

Intensity of exciting radiation = 7784 ergs. $p_H = 5.3$. Period of excitation of sol = 5 hours.

Wave-length	Length of soln.	Ellipticity developed on exposure to	
		<i>d</i> -light	<i>l</i> -light
5780\AA	4 cm	-0.15°	$+0.30^\circ$
5460	3	-0.30	$+0.60$
5200	2	-0.90	—
4916	0.5	-0.25	—

The above table shows that when the sol is excited in (*i.e.* exposed to) *d*-circularly polarised light, it develops a negative ellipticity which has a very high value at 5200\AA and 4916\AA . On the other hand, excitation of the sol in *l*-light results in the development of positive ellipticity which has a high value at 5460\AA . No optical rotation was found in both the cases. The dichroism that is developed does not change on keeping the sol for 24 hours.

Photoreduction.

Vanadic acid sol can be reduced by organic substances like tartaric acid, mandelic acid, etc., in visible light, vanadium being reduced from the pentavalent to the quadrivalent state: $V_2O_5 \rightarrow V_2O_4$. The colour change is from red or yellow to greenish black, blue or violet, depending upon the p_H .

The freshly prepared sol at $p_H 5.3$ was pre-excited (*i.e.* exposed to light before the reaction) in *d*- and *l*-light, and in each case the velocity of the reaction was found out in *d*- and *l*-light. Vanadic acid (as pentavalent vanadium) was estimated according to the method of Furman (*Ind. Eng. Chem.*, 1925, 17, 314). There is no dark reaction at $p_H 5.5$, and the photochemical reaction is zero-molecular with respect to vanadic acid,

The results obtained for the velocity of the photoreduction are given below. dx/dt refers to the number of g. mols. transformed per minute. *dl*-Tartrate is a mixture of *d*- and *l*-tartrates in equimolar proportions.

TABLE II.

Potassium tartrate = 0.10*M*. Radiation = whole visible. Vanadic acid sol = 0.05*M*. $p_H = 5.5$. Temp. = 25°. $I_{abs} = 1384$ ergs (in all cases). Period of excitation of sol = 5 hrs. Intensity of exciting radiation for sol = 7784 ergs.

Reductant.	Sol excited in <i>d</i> -light.	$dx/dt \times 10^4$ Reaction mixture exposed to <i>d</i> -light.		Sol excited in <i>l</i> -light.
<i>d</i> -tartrate	2.78	2.22	2.08	2.50
<i>l</i> - "	2.73	2.18	2.08	2.50
<i>dl</i> - "	2.78	2.22	2.04	2.50
<i>r</i> - "	2.78	2.22	2.13	2.55

The results show that when the sol is pre-excited in *d*-light, the velocity of the photoreduction of the sol is greater in *d*-light than in *l*-light; the reverse is the case when the sol is pre-excited in *l*-light, the velocity in *l*-light being greater than that in *d*-light. These velocity results are of the same type whether the reductant used is *d*- or *l*- or *dl*- or racemic-tartrate. It is clear, therefore, that at $p_H 5.5$, tartaric acid acts only as an acceptor for vanadic acid. The quantum efficiency is of the order of 0.4 (mean value).

The differences in velocity are in accordance with the dichroism exhibited by the sol on excitation. It must be mentioned here that the dichroism of the sol is not changed on being mixed with tartrate, the final concentrations being the same. When the sol is excited in *d*-light, the ellipticity developed is negative, i.e. $\epsilon_d > \epsilon_l$ (where ϵ_d and ϵ_l are the molecular extinction coefficients of the sol in *d*- and *l*-light respectively) (Rama Char, *loc. cit.*) a larger fraction of the incident *d*-light is absorbed by the surface layer of the sol particles and therefore, the velocity in *d*-light is expected to be greater than that in *l*-light. On the other hand, the ellipticity of the sol excited in *l*-light is positive, i.e. $\epsilon_l > \epsilon_d$, and the velocity in *l*-light is expected to be greater than that in *d*-light. Table I shows that the excited sol exhibits circular dichroism in the yellow, green and blue regions. It has been experimentally found that vanadic acid sol undergoes photoreduction by tartaric acid in these regions.

Table III gives the results obtained for the velocity of the photo-reduction of the dichroic sol in unpolarised (ordinary) light.

TABLE III.

Radiation = unpolarised light. Other conditions same as in Table II.

Excitation of sol.	$\frac{dx}{dt} \times 10^5$			
	d-tartrate.	l-tartrate.	dl-tartrate.	r-tartrate.
d-Circular	1.39	1.39	1.39	1.44
l "	1.39	1.39	1.39	1.44

The velocity of the reaction in unpolarised light is independent of the nature of the excitation of the sol used and also independent of the reductant.

The author wishes to express his thanks to Prof. J. C. Ghosh, for his kind interest and valuable suggestions during the investigation.

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Received June 23, 1941.

COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART III. COPPER AND NICKEL PHENYL-BIGUANIDINES AND THEIR DIFFERENT MODIFICATIONS.

BY PRIYADARANJAN RÂY AND KSHITISHRANJAN CHAKRAVARTY.

Copper phenylbiguanide, both hydrated and anhydrous, as well as many of its salts (*viz.* chloride, bromide, iodide, sulphate, dithionate, nitrate and nitrite) have been isolated in two forms, α and β , differing in colour, m.p. and solubility. The anhydrous copper phenylbiguanidines have been proved to be monomeric by ebullioscopic measurements. The α -chloride has been found to be transformed into the β -form at 101° in presence of steam. The conditions for transformation of the two varieties for other salts have also been determined. Besides, salts such as thiosulphate, thiocyanate, sulphite, chlorate, bromate and iodate have also been prepared only in one form and their properties studied.

The two varieties of copper phenylbiguanidine, its hydrate and salts, may be regarded as dimorphs or *cis-trans* isomers, but the balance of evidences seems to support the latter view.

Of the compounds studied, the β -base, the β -chloride and the β -sulphate have been described by previous workers.

Nickel phenylbiguanidine has been isolated in three forms, namely α , β and γ , differing in colour, solubility and other properties. The γ -variety is likely to be a solid solution or molecular compound of the α and β forms, the latter two possibly representing the *cis-trans* isomerides of the planar nickel complex. The idea of polymorphism also cannot be definitely excluded without further investigations.

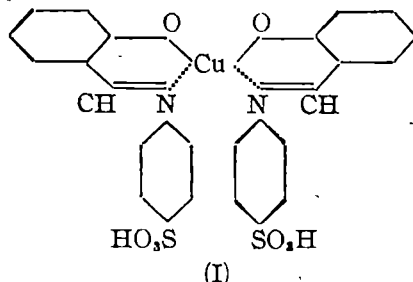
Various salts of nickel phenylbiguanide, such as the chloride, bromide, iodide, nitrate, nitrite, dithionate, sulphate, thiosulphate, sulphite, thiocyanate, chlorate, bromate and iodate have been prepared and their properties studied.

Of these nickel compounds the β -base, chloride and sulphate have been described by earlier workers.

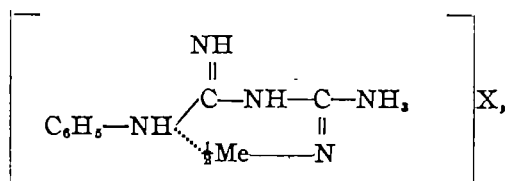
The planar configuration of the four co-ordinated inner-metallic complexes of bivalent nickel and copper has now been well established. Evidences in support of this are derived not only from the classical methods of stereochemistry but also from a substantial mass of physical data, specially relating to X-ray measurement of crystalline salts.

The occurrence of cis-trans isomerides of the nickel derivative of benzylmethylglyoxime (Sugden, *J. Chem. Soc.*, 1932, 246) is a definite illustration on the point. Cox, Wardlaw and collaborators (*ibid.*, 1935, 459, 1475) have demonstrated by means of X-ray studies the planar configuration for the 4-co-valent nickel. From the magnetic criterion of the bond type deduced from Pauling's theory (*J. Amer. Chem. Soc.*, 1931, 53, 1367) planar configuration with d-s-p² hybridisation is generally established for red and yellow nickel complexes like nickel dimethylglyoxime, nickel dicyandiamidine, potassium nickelocyanide, nickel biguanide etc., which are all diamagnetic (Rây and Bhar, *J. Indian Chem. Soc.*, 1928, 5, 499; Sugden, *J. Chem. Soc.*, 1939, 246). In the case of 4-co-valent copper complexes, however, magnetic data can offer no guidance as to their spatial configuration. All the simple and complex salts of bivalent copper possess similar paramagnetic properties. This follows directly from the electronic configuration of the cupric ion itself, which contains one unpaired electron in the fifth d-orbital. For the production of four equivalent hybrid d-s-p² bonds, giving rise to a planar configuration of the copper complex, this lone electron must be promoted to a higher level in order to make the fifth d-orbital available for bond formation; and this would make the complex paramagnetic like the cupric ion. Planar configuration for a number of copper complexes has been demonstrated by several workers with the help of X-ray measurements. Thus, cupric derivatives of β -diketones (Cox and Webster, *J. Chem. Soc.*, 1935, 731), copper phthalocyanin complex (Robertson, *ibid.*, 1935, 615), dipyridine cupric chloride (Cox, Sharatt, Wardlaw and Webster, *ibid.*, 1936, 129), cupric chloride dihydrate (Harkar, *Z. Krist.*, 1936, 93, 136) have all been found to possess planar structure. The isomorphism of 4-co-valent planar nickel complexes with the corresponding complexes of copper, *e.g.*, nickel and copper compounds of methylethylglyoxime, is a strong indication in favour of planar configuration for the latter. Planar trans-configuration for the salicylaldoxime and picolinate of copper also has been established by X-ray studies. But a definite stereochemical evidence on the point, leading to the isolation of cis-trans isomers of a 4-co-valent copper complex, is wanting. Recently Pfeiffer and Glaser (*J. prakt. Chem.*, 1939, ii, 153, 265) have made an observation that naphthaldehyde methylimine copper, besides giving dark brown needles of metallic lustre, can be crystallised under certain conditions to form long green needles. The green crystals were transformed into brown variety on heating to 140° or on keeping under methyl alcohol at the ordinary temperature. But the colour of the solution in pyridine of both varieties was identical. Pfeiffer and Krebs (*J. prakt.*

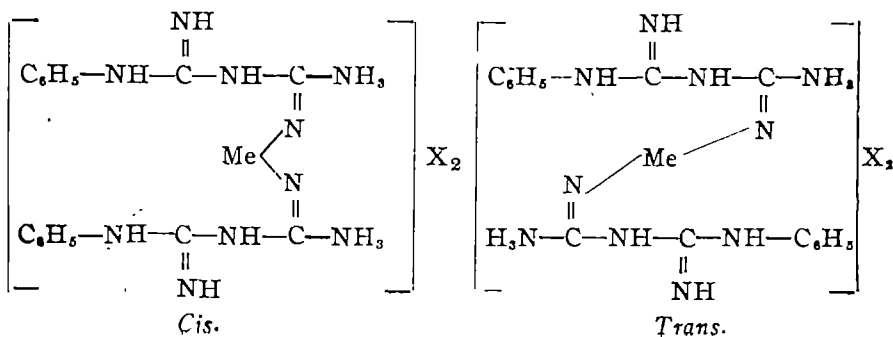
Chem., 1940, ii, 155, 77) also obtained two forms of sodium and barium salts of the acid (I), differing in their solubility in glycol or glycerine. Whether these represented real cases of *cis-trans* isomerism or dimorphism could not be decided by the authors.



Of the various 4-co-valent copper compounds so far studied only the *trans*-modifications could be isolated. All attempts to prepare the *cis*-form ended in failure. With a view to study the subject further, preparation of copper and nickel complexes with long-chain co-ordinating molecules was undertaken. Phenylbiguanide was selected as a suitable bidentate molecule for the purpose. Simple and substituted biguanides have been found by Rây and co-workers (*J. Indian Chem. Soc.*, 1937, 14, 670; 1938, 15, 353) to give fairly stable, well-defined, characteristic complexes with trivalent and bivalent metals like Cr, Co, Ni, Cu, etc. The constitution of the biguanide complexes with bivalent metals can be represented according to Rây and Saha (*loc. cit.*) by the following formula :



where X is a monovalent anion. This structure suggests the existence of two isomeric *cis* and *trans* forms :



We have been able to obtain a number of copper phenylbiguanide complexes in two modifications, *viz.* chloride, bromide, iodide, sulphate, nitrate, nitrite, dithionate and the free base. These might be called α - and β -forms. The α -form in each case differs considerably from the β -variety in solubility, melting point, colour (both in the hydrated and the anhydrous state) and rate of hydrolysis. Temperature and moisture accelerate the transformation of α - into β -variety.

The α -chloride is changed into the β -form at 101° in presence of steam, or when kept for a long time in contact with water, or by boiling. It crystallises with 6 molecules of water in the form of bluish violet crystals and when dehydrated retains the same colour. The β -chloride, which is prepared from slightly acidic solution at the boiling temperature, gives rise to light brick-red crystals and contains 3 molecules of water, the colour remaining unchanged on dehydration. The anhydrous α -chloride melts at 170° and the anhydrous β -chloride at 210° . The freshly prepared aqueous solution of the α -variety is violet-blue in colour and that of β -variety is reddish violet. The α -chloride is more soluble than the β -form. The α - and β -varieties of other salts and of complex base (both hydrated and anhydrous) also differ from each other in a similar way.

The two varieties may be regarded as *cis* and *trans* isomers of the planar copper complex, or as dimorphs or polymers. But the balance of evidences supports the first view.

Each variety (hydrated or anhydrous) retains its melting point and other properties unchanged on repeated crystallisation from water under the same condition. The α -variety changes into the β -form as stated above, but the β -form has never been found to change into the α -modification.

In aqueous solution they are all monomeric as indicated by cryoscopic and conductivity measurements. The α -chloride is much less dissociated at 0° than the β -chloride.

The aqueous solution of the α -chloride is quite stable and does not suffer any appreciable change by keeping at the room temperature for some days. The β -chloride, when dissolved in water, readily gives rise to the formation of a number of colloidal aggregates in solution as could be detected by ultramicroscope. Even after ultrafiltration of a solution of the β -chloride the filtrate is found to develop again a number of colloidal particles in a day or two. The absorption spectra of the aqueous solutions of the two chlorides after ultrafiltration were, however, found to be identical. An X-ray study of their crystals, therefore, would help to make a definite conclusion on the point.

As the β -variety appears to be more stable, since it is formed from slightly acid solution as well as by rise of temperature from the α -variety in presence of steam, it may reasonably be regarded to represent the *trans* modification, the α -form having the *cis* configuration.

In the case of nickel phenylbiguanide complexes only the base has been isolated in more than one form. These differ in their colour, solubility and decomposition temperature.

The α -nickel base is brick-red in colour and contains only $\frac{1}{2}$ molecule of water which is lost at 110° . It is insoluble in water, but soluble in alcohol and acetone changing rapidly into the yellow variety (γ). The same change occurs on keeping it in contact or on heating with water.

The β -nickel base is anhydrous and light yellow in colour. It is insoluble in water and all common organic solvents. On heating it decomposes at 265° , while the decomposition of the α -base occurs at 257° . On account of its greater stability it may be represented by the *trans* configuration. The α -form, therefore, represents the *cis* modification.

Besides these a third (γ) variety of yellow colour has also been prepared. This is very likely a molecular compound or mixed crystals of the α - and β -forms.

As none of the nickel phenylbiguanide salts, however, have been obtained in more than one form, no definite conclusion can be arrived at without further investigation, and the above representation regarding the different forms of the base as *cis-trans* isomers should be viewed as a tentative one. For they might as well be dimorphs or polymers.

A number of complex copper and nickel phenylbiguanide salts have been prepared and their properties studied. Generally, the solubility of nickel complex was found to be much less than that of their corresponding copper compounds. The sulphate, iodate, bromate, chlorate and dithionate of nickel compounds were found to be very sparingly soluble in water at the ordinary temperature.

The following compounds have been prepared and described in this paper.

Copper. The free base, hydrated and anhydrous in two forms— α and β ; the chloride, bromide, iodide, nitrite, nitrate, sulphate and dithionate in α - and β -forms, besides the thiosulphate, thiocyanate, chlorate, bromate, iodate and sulphate.

Of these, the dark rose base (β), the red chloride (β), the rose-coloured sulphate (β) and the chromate have been described by previous workers (Smolka and Friedrich, *Monatsh*, 1888, 9, 227).

Nickel. The free base in three forms (α , β and γ), the chloride, bromide iodide, sulphate, iodate, nitrate, nitrite and sulphocyanide. Of these the free base (β), chloride and sulphate have already been described before (Smolka and Friedrich, *loc. cit.*).

EXPERIMENTAL.

I. Copper Compounds.

α -Copper Phenylbiguanidine and its Hydrate.—The hydrate was precipitated in the form of light pink, finely divided crystals by adding a concentrated solution of caustic soda in excess to a cold concentrated solution of α -copper phenylbiguanide hydrochloride. This was rapidly filtered by suction, washed with cold water and dried on a porous plate. On keeping in contact with water at the ordinary temperature it changes into the rose-red β -form. It liberates ammonia from hot ammonium chloride solution. {Found: N, 31.20; Cu, 14.05. $[\text{Cu}(\text{PhBigH}^+)_2](\text{OH})_2$ requires N, 31.0; Cu, 14.06; H_2O , 7.97}. $\text{PhBigH} = \text{C}_6\text{N}_4\text{H}_{11}$ = one molecule of phenyl biguanide.

The substance loses 7.9% of its weight at 100°–110°. {Found: Cu, 15.10. $\text{Cu}(\text{PhBig})_2$ requires Cu, 15.28 per cent}.

The anhydrous base possesses the same colour as the hydrated variety. The substance is soluble in methyl and ethyl alcohol and also in acetone, but is insoluble in chloroform or benzene. M. p. (decom.) 155°.

The molecular weight of the anhydrous substance determined by the boiling-point method in methyl alcoholic solution, gave a value of 382.3 showing its monomeric nature. Calc. M. W. = 415.5.

β -Copper Phenylbiguanide and its Hydrate.—The β -hydrate was prepared by adding a concentrated solution of caustic soda to a hot solution of α -copper phenylbiguanide hydrochloride. The mixture was allowed to cool and the precipitated base was filtered and washed with water. The product was dried over caustic soda. {Found: N, 31.1; Cu, 14.0. $[\text{Cu}(\text{PhBigH}^+)_2](\text{OH})_2$ requires N, 31.0; Cu, 14.06; H_2O , 7.97 per cent}.

Loss at 118° = 7.9 per cent. {Found: Cu, 15.20; $\text{Cu}(\text{PhBig})_2$ requires Cu, 15.28%}.

Both hydrated and the anhydrous base form finely divided dark red crystals, insoluble in water. The anhydrous base melts at 165°. It appears to be more soluble than the α -variety in alcohol and acetone.

Molecular weight of the anhydrous base by ebullioscopic method in methyl alcoholic solution was found to be 386.2, showing that it is monomeric. Calc. M. W. = 415.5.

α -Copper Phenylbiguanidinium Chloride.

The compound can be prepared in several ways.

(i) By treating an aqueous solution of phenylbiguanide base with a solution of cupric chloride.

(ii) By treating a hot solution of phenylbiguanide hydrochloride with an ammoniacal cupric chloride solution.

(iii) By heating a solution of ammonium chloride with α -copper phenylbiguanide until the evolution of ammonia ceases.

(iv) By digesting freshly precipitated copper hydroxide with a solution of phenylbiguanide hydrochloride on water-bath. This method was usually adopted for the preparation of the substance.

On concentrating and cooling the filtrate from copper hydroxide (method, iv) blue-violet crystals of copper phenylbiguanide hydrochloride separated out. The product was purified by recrystallisation at 60-70° and dried in air. {Found: N, 23.37; Cl, 11.86; Cu, 10.70. $[\text{Cu}(\text{PhBigH}^+)_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ requires N, 23.50; Cl, 11.90; Cu, 10.66 per cent}.

Loss of water at 110° = 18.04%. Calc.: H_2O 18.10%.

The anhydrous chloride retains the colour of the original hydrated substance. (Found: Cu, 13.0. Calc.: Cu, 13.02 per cent).

Solubility at 28° = 2.1088 g. of the hydrated chloride per 100 g. of the solution. M p (anhydrous salt), 170° (decomp.).

The hydrated chloride also melts at 170° on slowly heating. But on rapid heating or sudden immersion in a hot bath at 100°, the hydrate first forms a frothy mass, then solidifies with rise of temperature and finally melts at 210°, which is the melting point of β -copper phenylbiguanide hydrochloride. This suggests the transformation of α -form into the β -variety under the conditions of the experiment, i.e., rise of temperature and presence of steam. On the other hand, if the α -hydrated chloride is gradually heated to make it anhydrous, it does not change into β -variety on further rise of temperature. Rise of temperature in presence of steam is, therefore, a necessary condition for its transformation into the anhydrous β -variety. This can be demonstrated by actual experiment and the transition temperature thus determined was found to lie between 102° and 103°. Even at the ordinary temperature the α chloride changes slowly into the β -form on keeping in contact with water for several days.

Equivalent conductivity at 28°.

v (dilution in litres) ...	32	64	128	256	512	1024
λ_v ...	89.1	102.2	105.7	109.04	112.2	115.4
λ_∞ (mean) ...	117.9 from Walden's formula $\lambda_\infty = \lambda_v(1 + v_1 \cdot n_1 \cdot 0.692 \cdot v^{-\frac{1}{2}})$					

where n_1 and n_2 are the valencies of the cation and anion respectively (Walden. "Leitvermögen der Lösungen," 1924, **V**, 53). The mobility of $\text{Cu}(\text{PhBigH}^+)_2 = 117.9 - 79.5 = 38.4$, the ionic mobility of chlorine at 28° being 79.5.

Cryoscopic measurement.

Substance in 100 g. water (on the anhydrous basis).	Depression in $^\circ\text{C}$. Δ .	M W. (found) m .	Vant Hoff's factor $i = \frac{M \text{ (calc.)}}{m}$.	Degree of dissociation $\alpha = 1 - 1/n - 1$ ($n = 3$).
1.3080 g.	0.12	202.7	2.40	0.70

The β -Chloride.—A concentrated solution of the α -chloride was heated to boiling and acidified distinctly with hydrochloric acid. The solution was then almost neutralised with caustic soda solution and boiled further for about 1 minute. It was then filtered hot and the filtrate heated once more and then allowed to cool. On keeping overnight, the β -chloride separated out in the form of red crystals. These were purified by recrystallisation and dried in air. {Found; N, 25.83; Cl, 12.90; Cu, 11.75; H_2O (loss at 110°), 9.60. $[\text{Cu}(\text{PhBigH}^+)_2] \text{Cl}_2 \cdot 3\text{H}_2\text{O}$ requires N, 25.80; Cl, 13.08; Cu, 11.72; H_2O , 9.95 per cent}.

For the anhydrous salt (Found: Cu, 12.95. Calc.: Cu, 13.02%).

Smolka and Friedrich (*loc. cit.*) described a carmine-red chloride containing $1\frac{1}{2} \text{H}_2\text{O}$ only.

The solubility of the β -chloride (hydrated) at 28° is considerably less than that of the α -chloride and is equal to 1.6055 g. per 100 g. of solution. The anhydrous compound retains the colour of the original hydrate; m.p. (both hydrated and anhydrous), 210° .

A freshly prepared solution of the β chloride is red-violet and is found to contain a number of colloidal aggregates when examined under the microscope. After ultrafiltration the colour of the solution becomes identical (blue-violet) with that of the α -chloride, but turns red-violet again in a day or two. The phenomenon is possibly connected with its increased tendency to hydrolysis.

Equivalent conductivity at 28° .

v (litres)	...	32	64	128	256	512	1024
λ_v	...	92.98	94.84	100.9	107.2	110.9	114.8
λ_∞ (mean)=		117.5					

Cryoscopic measurement.

Substance in 100 g. water (on the anhydrous basis).	Depression in °C Δ .	M W. (found) m .	Vant Hoff's factor $i = \frac{M \text{ (calc.)}}{m}$	Degree of dissociation $\alpha = i - 1/n - 1$ ($n = 3$).
0.9830 g.	0.105	174.1	2.80	.90

The degree of dissociation is much higher than that of the α -variety (0.74).

The α -Bromide.—This was prepared by adding a concentrated solution of potassium bromide to a cold concentrated solution of the complex α -chloride. This was filtered, washed with water and dried on a porous plate. It forms finely divided, light pink coloured crystals. {Found : N, 22.89 ; Br, 26.20 ; Cu, 10.28. $[\text{Cu}(\text{PhBigH}^+)_2]\text{Br}_2, 2\text{H}_2\text{O}$ requires N, 22.80 ; Br, 26.08 ; Cu, 10.30 per cent}. Solubility at $28^\circ = 1.71$ g. per 100 g. of the solution.

When the α -bromide was kept in contact with its solution at the ordinary temperature, it gradually changed into the deep rose-coloured β -bromide. The same transformation occurs on keeping the moist α -bromide for some days.

The β -Bromide.—When the α -bromide was kept in contact with its solution in a beaker for 3-4 days, it completely changed into the deep rose-red β -variety. This was washed with water and dried in air. {Found : Br, 26.21 ; Cu, 10.20. $[\text{Cu}(\text{PhBigH}^+)_2]\text{Br}_2, 2\text{H}_2\text{O}$ requires Br, 26.08 ; Cu, 10.30 per cent}. Solubility at $28^\circ = 1.55$ g. in 100 g. of the solution.

The α -Iodide was precipitated in the form of finely divided, light pink crystals by adding a concentrated solution of potassium iodide in excess to that of the α -chloride in the cold. The precipitate was washed with water and dried on a porous plate. On boiling with water it changes into the brown β -form: {Found : N, 19.77 ; I, 35.90 ; Cu, 9.01. $[\text{Cu}(\text{PhBigH}^+)_2]\text{I}_2, 2\text{H}_2\text{O}$ requires N, 19.79 ; I, 35.88 ; Cu, 8.97 per cent}.

The β -iodide was prepared by heating the α -iodide with water to 100° and then keeping the mixture overnight. The product was washed with water and dried in air. It forms brown coloured crystals, difficultly soluble in water. {Found : I, 35.60 ; Cu, 8.90. $[\text{Cu}(\text{PhBigH}^+)_2]\text{I}_2, 2\text{H}_2\text{O}$ requires I, 35.88 ; Cu, 8.97 per cent}.

The α -nitrate was obtained as a violet coloured, crystalline precipitate by adding a cold concentrated solution of potassium nitrate to that of α -chloride, cooled in ice. The precipitate was washed with cold water, dried first on a porous plate and then over concentrated H_2SO_4 . {Found : Cu, 11.70 ; NO_3 , 22.60. $[\text{Cu}(\text{PhBigH}^+)_2](\text{NO}_3)_2$ requires Cu, 11.72 ; NO_3 , 22.89 per cent}. Solubility at $28^\circ = 0.4988$ g. in 100 g. of the solution.

When kept in contact with its solution it gradually changed into the red β -form in 3 to 4 days.

Equivalent conductivity at 28°.

v (litres)	...	64	128	256	512	1024
λ_v		92'21	98'5	100'9	103'6	108'9
λ_∞ (mean)	...	110'5				

The β -nitrate was prepared from the α -variety by keeping it in contact with water for 7 days when a complete change into the red β -form occurs. {Found: Cu, 11'39; NO₃, 21'77. [Cu(PhBigH)⁺₂](NO₃)₂, H₂O requires Cu, 11'36; NO₃, 22'16 per cent}. Solubility at 28° = 0'2923 g. in 100 g. of the solution.

The α -sulphate was obtained as a sparingly soluble, pink coloured crystalline precipitate by adding a concentrated solution of potassium sulphate in excess to that of the α -chloride, washed and dried as usual. When heated with water it changes into the violet-red β -form. {Found: Cu, 10'92; SO₄, 16'71. [Cu(PhBigH⁺)₂SO₄], 4H₂O requires Cu, 10'84; SO₄, 16'40 per cent}.

The β -sulphate was prepared by heating the α -sulphate with water to 100° and keeping the product overnight. It forms sparingly soluble, violetred crystals. {Found: N, 23'11; Cu, 10'45; SO₄, 16'20. [Cu(PhBigH⁺)₂]SO₄, 5H₂O requires N, 23'19; Cu, 10'53; SO₄, 15'9 per cent}.

Smolka and Friedrich (*loc. cit.*) have described a rose-red sulphate with 1½ H₂O.

The α -nitrite was prepared by adding a cold concentrated solution of sodium nitrite to that of the α -chloride, cooled in ice. The red-violet precipitate was allowed to settle, filtered by suction, washed with ice-cold water and dried on a porous plate. It is very unstable in the moist state and changes rapidly at the room temperature into the β -form. {Found: Cu, 12'05; NO₂, 17'30. [Cu(PhBigH⁺)₂](NO₂)₂, H₂O requires Cu, 12'05; NO₂, 17'44 per cent}. Solubility at 28° = 0'096 g. per 100 g. of the solution.

The β -nitrite was prepared by keeping the α -nitrite in contact with water for a day or two till complete transformation occurs. It forms dark violet crystals, sparingly soluble in water. It is nearly 50% less soluble than the α -form. {Found: Cu, 12'44; NO₂, 18'05. [Cu(PhBigH⁺)₂](NO₂)₂ requires Cu, 12'47; NO₂, 18'05 per cent}. Solubility at 28° = 0'0457 g. per 100 g. of the solution.

The α -dithionate was obtained from a concentrated solution of sodium dithionate and that of the α -chloride. The light pink-coloured precipitate was washed with water, dried first on a porous plate and then in a desiccator over H_2SO_4 . When heated with water it changes into the red β -form. {Found: Cu, 11.0; S_2O_6 , 28.0. $[\text{Cu}(\text{PhBigH}^+)_2]\text{S}_2\text{O}_6$ requires, Cu, 10.99; S_2O_6 , 27.70 per cent}.

The β -dithionate was prepared by heating the α -variety with a little water and keeping the product overnight. This was washed with water and dried in air. The substance forms red crystals, sparingly soluble in water. {Found: Cu, 10.68; S_2O_6 , 27.0. $[\text{Cu}(\text{PhBigH}^+)_2]\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$ requires Cu, 10.66; S_2O_6 , 26.88 per cent}.

Copper phenylbiguanidinium sulphite was obtained as a dark violet crystalline precipitate by adding a concentrated solution of the α -chloride to that of sodium sulphite. The product was washed with water and dried in air. {Found: N, 23.55; Cu, 10.70; SO_3 , 14.05. $[\text{Cu}(\text{PhBigH}^+)_2]\text{SO}_3 \cdot 5\text{H}_2\text{O}$ requires N, 23.80; Cu, 10.80; SO_3 , 13.60 per cent}.

The thiosulphate was prepared by adding a concentrated solution of sodium thiosulphate to that of the complex α -chloride. The light blue, crystalline precipitate was washed with water and dried in air. {Found: N, 24.80; Cu, 11.20; S_2O_3 , 19.95. $[\text{Cu}(\text{PhBigH}^+)_2]\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ requires N, 24.75; Cu, 11.24; S_2O_3 , 19.80 per cent}.

The thiocyanate was obtained from a concentrated solution of ammonium thiocyanate and that of the α -chloride. The pink coloured crystalline precipitate was washed and dried as usual. {Found: N, 30.40; S, 11.71; Cu, 11.50. $[\text{Cu}(\text{PhBigH}^+)_2](\text{SCN})_2 \cdot \text{H}_2\text{O}$ requires N, 30.40; S, 11.60; Cu, 11.53 per cent}.

The chlorate was prepared from a concentrated solution of potassium chlorate and that of the complex chloride. The pink coloured crystalline precipitate was washed with water and dried over H_2SO_4 in a desiccator. The dry salt explodes on rubbing in a mortar. {Found: Cu, 10.85; ClO_3 , 28.20. $[\text{Cu}(\text{PhBigH}^+)_2](\text{ClO}_3)_2$ requires Cu, 10.85; ClO_3 , 28.56 per cent}.

The bromate was obtained from potassium bromate and the α -chloride as in the previous case. It forms pink coloured crystals and explodes like the chlorate when ground in a mortar. {Found: Cu, 9.48; BrO_3 , 37.87. $[\text{Cu}(\text{PhBigH}^+)_2](\text{BrO}_3)_2$ requires Cu, 9.43; BrO_3 , 38.0 per cent}.

The iodate was obtained as violet crystals from potassium iodate and the complex chloride. This was washed and dried as in the previous case. {Found: Cu, 8.22; IO_3 , 44.79. $[\text{Cu}(\text{PhBigH}^+)_2](\text{IO}_3)_2$ requires Cu, 8.27; IO_3 , 45.60 per cent}.

Nickel Compounds.

α-Nickel Phenylbiguanidine and its Hydrate.—To a cold (8° - 10°) concentrated solution of nickel phenylbiguanide hydrochloride a cold concentrated solution of caustic soda was rapidly added in excess. The red precipitate was immediately washed with ice-cold water, dried first on a porous plate and then over caustic potash. {Found: N, 33'09; Ni, 13'88 Ni(PhBig)₂. $\frac{1}{2}$ H₂O requires N, 33'36; Ni, 13'99 per cent}.

When heated to 110° for 2 hours it lost 2% of its weight without any change of colour. Calc. H₂O, 2'14 per cent.

[Found for anhydrous product: Ni, 14'11. Calc.: Ni, 14'22 per cent].

The substance is soluble in methyl alcohol, ethyl alcohol and also in acetone forming an orange-red solution, but rapidly separates out in the form of a yellow powder (β -variety). The same change is also observed to occur in the moist state. It decomposed at 255° without melting.

β-Nickel phenylbiguanidine was precipitated as a light yellow, crystalline powder by adding a concentrated solution of caustic soda to a warm solution of the hydrochloride. This was washed with water and dried over caustic soda. {Found: N, 33'73, Ni, 14'12 Ni(PhBig)₂ requires N, 34'09; Ni, 14'22 per cent}.

The substance is insoluble in alcohol, acetone or water, and decomposes, without melting at about 265° . The compound has also been described by Smolka and Friedrich (*loc. cit.*).

γ-Nickel Phenylbiguanidine and its Hydrate.—This was prepared by keeping the moist α -variety at the room temperature, when after 2 to 3 days the mass changed completely into a deep yellow product. This was dried over caustic soda. {Found: N, 33'10; Ni, 13'93; H₂O, (by loss at 110°) 2'04. Ni(PhBig)₂, $\frac{1}{2}$ H₂O requires N, 33'36; Ni, 13'99; H₂O, 2'14 per cent}.

There was no change of colour on dehydration.

The anhydrous product gave Ni, 14'17; Calc. 14'22 per cent. The substance is insoluble in alcohol, acetone or water and decomposes without melting at 263° . This is likely to be a molecular compound or solid solution of α - and β -variety.

Nickel phenylbiguanidinium chloride can be prepared by any of the following methods.

(a) By the action of phenylbiguanide hydroxide on a solution of nickel chloride.

(b) By adding a solution of ammoniacal nickel chloride to that of phenylbiguanide hydrochloride.

(c) It was, however, prepared by digesting a solution of phenylbiguanide hydrochloride with excess of freshly prepared nickel hydroxide. The mixture was filtered hot. The filtrate on concentration and cooling deposited golden yellow crystals of nickel phenylbiguanidinium chloride. These were purified by recrystallisation either from water or from absolute alcohol and dried in air. {Found: N, 26'30; Cl, 13'20; Ni, 11'08; H₂O (by loss at 110°), 8'43. [Ni (PhBigH⁺)₂]Cl₂, 2½H₂O requires N, 26'50; Cl, 13'43; Ni, 11'12; H₂O, 8'52 per cent}.

The anhydrous chloride gives Ni, 12'11; Calc. Ni, 12'14 per cent.

Smolka and Friedrich (*loc. cit.*) have also described the anhydrous chloride.

The *bromide* was obtained as a bright yellow crystalline precipitate by adding a hot concentrated solution of potassium bromide to that of the complex chloride. This was washed with water and dried in air. {Found: N, 22'80; Br, 26'20; Ni, 9'80. [Ni(PhBigH⁺)₂]Br₂, 2H₂O requires N, 23'0, Br, 26'28; Ni, 9'64 per cent}.

The *iodide* was prepared from potassium iodide and the complex chloride as described above. The sparingly soluble, yellow crystals of the iodide were washed and dried as usual. {Found: N, 20'30; I, 37'0; Ni, 8'59. [Ni(PhBigH⁺)₂]I₂, H₂O requires N, 20'44; I, 37'09; Ni, 8'57 per cent}.

The *dithionate* was obtained from concentrated solutions of sodium dithionate and the complex chloride. On cooling, the dithionate separated in the form of yellow crystals. {Found: N, 24'40; Ni, 10'23; S₂O₆, 28'13. [Ni (PhBigH⁺)₂] S₂O₆ requires N, 24'48; Ni, 10'25; S₂O₆, 27'95 per cent}.

The *thiosulphate* was obtained from an excess of a concentrated solution of sodium thiosulphate and that of the complex chloride. The yellow crystalline precipitate was washed and dried as usual. {Found: N, 26'50; Ni, 11'17; S₂O₃, 21'53. [Ni(PhBigH⁺)₂] S₂O₃ requires N, 26'68; Ni, 11'18; S₂O₃, 21'33 per cent}.

The *nitrate* separated in the form of finely divided, bright yellow crystals on cooling a mixture of concentrated solutions of potassium nitrate and the complex chloride. {Found: Ni, 10'50; NO₃, 22'50. [Ni(PhBigH⁺)₂] (NO₃)₂, H₂O requires Ni, 10'58; NO₃, 22'35 per cent}.

The *sulphate* was obtained as yellow crystals by precipitating a concentrated solution of the complex chloride with that of potassium sulphate. {Found: Ni, 10'70; SO₄, 17'70. [Ni(PhBigH⁺)₂]SO₄, 2H₂O requires Ni, 10'77; SO₄, 17'61 per cent}.

The sulphate has also been described by Smolka and Friedrich (*loc. cit.*), which, however, contains 1½ H₂O only.

The sulphite.—A concentrated solution of sodium sulphite in excess was added to a hot concentrated solution of the complex chloride. On cooling, the yellow crystals of the sulphite gradually separated out. {Found: Ni, 11'53; SO₃, 15'75. [Ni(PhBigH⁺)₂]SO₃, H₂O requires Ni, 11'50; SO₃, 15'65 per cent}.

The chlorate was obtained as a light yellow, crystalline precipitate by adding an excess of a concentrated solution of potassium chlorate to that of the complex chloride. {Found: Ni, 10'10; ClO₃, 28'20. [Ni(PhBigH⁺)₂](ClO₃)₂ requires Ni, 10'14; ClO₃, 28'8 per cent}.

The bromate was obtained as sparingly soluble, orange coloured crystals from a concentrated solution of potassium bromate and a hot concentrated solution of the complex chloride. {Found: Ni, 8'72; BrO₃, 37'92. [Ni(PhBigH⁺)₂](BrO₃)₂ requires Ni, 8'77; BrO₃, 38'27 per cent}.

The iodate was obtained as orange-red, crystalline precipitate by adding a concentrated solution of potassium iodate to that of the complex chloride. {Found: Ni, 7'31; IO₃, 43'54. [Ni(PhBigH⁺)₂](IO₃)₂, 2H₂O requires Ni, 7'34; IO₃, 43'82 per cent}.

The thiocyanate was prepared as a yellow crystalline precipitate by adding a concentrated solution of potassium thiocyanate to that of the complex chloride. {Found: N, 32'22; S, 12'21; Ni, 11'05. [Ni(PhBigH⁺)₂](SCN)₂ requires N, 31'78; S, 12'10; Ni, 11'10 per cent}.

The nitrite was obtained from a concentrated solution of sodium nitrite and that of the complex chloride. It forms sparingly soluble, orange-yellow crystals. {Found: Ni, 11'15; $\frac{2}{3}$ NO₂, 18'0. [Ni(PhBigH⁺)₂](NO₂)₂, H₂O requires Ni, 11'23; NO₂, 17'60 per cent}.

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Received September 3, 1941.

ELECTROCHEMICAL PRÉPARATION OF SODIUM CHLORATE FROM AQUEOUS SODIUM CHLORIDE.

BY SRIDHAR SARVOTTAM JOSHI AND K. SRINIVASAN.

A detailed study has been made of the electrolytic production of chlorate by the electrolysis of sodium chloride solution. Data are given in respect of the influence on the current efficiency of chlorate formation of the following factors : the temperature, the separation and disposition of the electrodes, the electrolyte concentration, the current density and addition agents. Influence of sun light and superimposition of A C during the electrolysis have also been investigated. A general theory of chlorate formation, *electrochemically*, is discussed.

Desite the fact that alkali chlorates are of very great commercial importance and especially as a war material, no systematic and detailed data are available in the literature in regard to the various factors involved in their preparation, electrochemically, which is increasingly superceding other well known methods. The present work was undertaken to study the efficiency of an experimental 'chlorate cell' over a certain range of conditions.

EXPERIMENTAL.

The cell consisted of a cylindrical glass vessel 6" in height and about 2" in diameter. It was closed with a well fitting cork which carried a platinum anode, a graphite cathode, a thermometer and an exit tube for the evolved gases. The temperature of the cell was controlled by immersion in a thermostat kept at the appropriate temperature. A fixed volume, *viz.*, 100 c.c. of NaCl solution of known concentration represented the bath ; to this was added 0.4 g. of $K_2Cr_2O_7$ in all experiments except those reported in Table V showing the influence of the various "*addition agents*" on the efficiency of the chlorate formation. The circuit included an ammeter, an adjustable resistance and voltmeter between the electrodes. After electrolysis, a known volume of the solution was analysed for (i) chlorate and (ii) total available chlorine *i.e.*, free chlorine and that present as hypochlorite which was determined by titration against a standard sodium arsenite solution. The current efficiency was calculated in respect of (i). These results and also those for (ii) are returned in the following tables, which illustrate the influence of such factors as the temperature (Table I), '*separation*' or the

inter-electrode distance, the vertical and horizontal disposition of the electrodes (Table II), initial concentration (Table III) and current density (Table IV), and 'addition agents' (Table V).

TABLE I.

Current=1.5 amp. Distance between the electrodes=2 cm.

Current density=1 amp./sq. cm. Current passed for 1 hour.

No.	Temp.	P. D. applied.	Strength of available Cl_2 in c.c of arsenite soln.	Current efficiency of chlorate formation.
1	30°	5 volts.	2.3	32.69%
2	40	5	2.0	51.93
3	50	4.8	1.7	57.95
4	60	4.8	1.4	71.68
5	70	4.7	1.1	86.02
6	80	4.7	0.9	91.75
7	90	4.6	0.7	96.24

TABLE II.

Variation of current efficiency with the separation of electrodes.

Current=1 amp. Temp.=50° Current density=0.667 amp./sq. cm.

Current passed for 2 hours.

Separation of electrodes	Voltage.	Strength of available Cl_2 in c.c of arsenite soln.	Current efficiency of chlorate formation	Separation of electrodes.	Voltage.	Strength of available Cl_2 in c.c of arsenite soln.	Current efficiency of chlorate formation
Both the electrodes horizontal.				Both the electrodes vertical.			
1 cm.	5.4	2.2	57.45%	1 cm.	4.5	0.9	77.19%
2	5.6	2.8	59.12	2	4.5	1.3	82.11
3	5.7	3.1	60.85	3	4.6	1.4	83.75
4	5.7	4.0	64.93	4	4.7	1.5	84.57
5	5.7	4.0	71.45	5	4.7	1.6	87.03
6	5.9	3.6	65.75	6	4.8	1.6	82.93
7	5.9	3.8	61.59	7	4.8	1.6	80.47
8	6.0	4.1	59.12	8	4.8	1.6	79.66

Evidently the current efficiency is greater with electrodes vertical than when they are horizontal.

TABLE III.

Variation of current efficiency with the initial concentration of sodium chloride.

Current strength = 1 amp. Current density = 0.667 amp./sq. cm.
Current passed for 2 hours.

Conc. of sodium chloride	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation.
5%	1.3	75.54%
10	1.4	75.54
15	1.4	77.34
20	1.5	79.66
25	1.6	80.46
Saturated	1.6	92.94

TABLE IV.

Variation of current efficiency with the current density.

Temp. = 60°. Distance between the electrodes = 2 cm. Quantity of electricity passed = 2 ampere-hours.

Anodic current density in amp per sq. cm.	Cathodic current density in amp. per sq. cm.	Strength of available Cl ₂ in c.c. of arsenite soln.	Current efficiency of chlorate formation.
2	1	1.35	64.88%
1	1	1.3	61.63
0.667	1	1.25	60.01
0.5	1	1.25	59.18
0.25	1	1.2	58.28
1	2	1.3	60.01
1	1	1.3	61.63
1	0.4	1.2	63.25
1	0.25	1.2	64.06
1	0.136	1.2	65.69

TABLE V.

The effect of addition agents on the current efficiency.

Current strength = 1 amp. Temp. = 50°. Current density = 0.667
amp./sq.cm. Current passed for 2 hours.

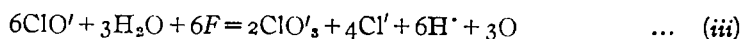
Addition agent.	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation	Addition agent.	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation
	0.8	48.45%	CaCl ₂	1.7	57.69%
K ₂ Cr ₂ O ₇	2.3	80.46	Dd(NO ₃) ₃	0.9	53.55
KMnO ₄	2.4	77.18	RbCl	0.7	48.45
YtCl ₃	0.6	76.38	CsCl	0.8	48.45
Na ₂ WO ₄	1.2	75.54	V ₂ O ₅	1.7	45.16
NH ₄ VO ₃	1.2	72.38	ThCl ₄	0.9	40.24
CeCl ₃	1.2	67.86	TlCl	0.8	27.92
UO ₂ (NO ₃) ₂	1.3	65.69	(NH ₄) ₂ MoO ₄	0.5	20.52
Zr(SO ₄) ₂	0.6	61.89	MnCl ₂	0.8	9.85
LaCl ₃	1.5	61.59	FeCl ₃	0.9	6.38
MgCl ₂	1.9	60.72	Ti(SO ₄) ₂	2.6	5.61
V ₂ O ₅	3.0	59.72			

DISCUSSION.

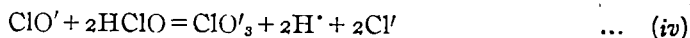
When a solution of an alkali chloride is electrolysed, hydrogen is liberated at the cathode and chlorine at the anode because of the high overvoltage necessary for the continuous discharge of OH' ions. If the electrodes are near each other and the anodic and cathodic solutions allowed to mix freely, the chlorine forms hypochlorite by secondary reactions with the OH' ions:



The concentration of the hypochlorite is, however, kept below a certain equilibrium value because it is used up in a number of side-reactions, the chief among which are (a) reduction at the cathode, (b) discharge of the ClO' ion at the anode and (c) chemical formation of the chlorate. The hypochlorite ion has a much lower discharge potential than the chloride ion (Foerster and Muller, *Z. Elektrochem.*, 1902, 8, 634) and is therefore, preferentially discharged. In an alkaline solution all the hypochlorite is ionised; the whole of it, therefore, can be discharged. In acid solutions, however, proportion of the ClO' ions is very low as the hypochlorous acid is a very weak one and its ionisation is further suppressed by the free acid present. In an acid solution with a high concentration of the chloride, the discharge of ClO' ions is expected to be very much smaller than that of the Cl' ions. The discharged ClO' ions, however, are converted into chlorate with the liberation of oxygen (Foerster and Muller, *Z. Elektrochem.*, 1902, 8, 665).



The chemical transformation of hypochlorite into chlorate can take place only in slightly acidified solutions because it is a reaction between the hypochlorite ion and the free hypochlorous acid (Foerster and Jorre, *J. prakt. Chem.*, 1899, 59, 53).

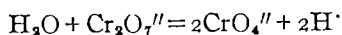


If the hypochlorite is converted into the chlorate by the electrochemical reaction (iii), then it requires 6 faradays of electricity more for 2 molecules of the chlorate. If the conversion is effected by the thermochemical reaction (iv), no electricity is used up and the formation of each molecule of the chlorate requires only 6 faradays necessary for producing 3 molecules of the hypochlorite. But the electrochemical conversion requires 9 faradays per molecule and so there is a relative reduction in efficiency of 33.3%. Usually in any process of electrolytic oxidation, oxygen evolution at the anode causes a loss in efficiency. According to the earlier workers, if the main reaction occurring at the anode is the electrochemical formation of ClO_3' ion by the oxidation of ClO' ions according to equation (iii), there will be a loss in efficiency of 33.3% corresponding to a loss of $\frac{1}{3}$ of the total active oxygen.

To get 100% efficiency, therefore, it is necessary to prevent reaction (iii) from occurring and increase the speed of reaction (iv). A slight acidification and a high concentration of chloride should serve the purpose.



because, the hypochlorous acid being a weak acid will not be ionised in amounts sufficient to permit the discharge of ClO' ions to any appreciable extent and by the law of mass action, speed of the reaction (iv) will be proportional to the square of the concentrations of free hypochlorous acid. There are of course other considerations which determine the acidity. A high acidity means a low solubility of chlorine and prevention of reaction (i) and (ii). So a good amount of the chlorine will escape. Moreover, free hypochlorous acid being volatile, much of it will be lost, especially at higher temperatures. The protective film formed by the dichromate will dissolve if the acidity increases. So the acidity is not allowed to rise and is kept within the required range by the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ which acts as a buffer [Pamfilov, *Bull. Inst. Polyt. Ivanovo. Voznesensk*, 1921, 4, 113).



Owing to the weakness of the hypochlorous acid very slight acidity is sufficient to suppress the formation of ClO' ions. The dichromate is also the best 'addition agent' found so far, for the prevention of cathodic reduction in chlorate cells. The effect of variation of temperature on the current efficiency is shown in Table I. Since acidic solutions have been used throughout, formation of the chlorate comes about chiefly by the thermochemical reaction (iv) and so the yield increases with temperature. But at higher temperatures the increase is not so great; so there must be some other factors which decrease the yield and the effects of which are much more pronounced at higher temperatures. The increased discharge of ClO' and OH' ions due to decrease in the oxygen overvoltage at high temperatures and the volatility of the free hypochlorous acid may act in this direction. Due to the fall in overvoltage and the greater conductivity at higher temperatures the voltage is less.

No adequate information is available in the literature to show the effect of the variation of the interelectrode distance in chlorate cells. It has been taken for granted that the electrodes must be as near each other as possible. But the results given in Table II go to show that there exists an optimum distance of maximum yield. Unless the solution is very vigorously stirred, there will be formed a zone where the anodic and cathodic solutions meet and react to form the hypochlorite. From this zone the ClO' ions would move towards the anode and get discharged if in the meanwhile they do not react chemically. So the farther away the neutral zone from the anode, the less will be the discharge of ClO' ions and so the loss in efficiency will be comparatively small. But when the separation

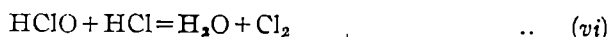
becomes great, the chlorine not finding a sufficiency of OH' ions escapes and produces a loss. So there is a region of optimum efficiency where the combined loss due to these two causes is at a minimum.

The effect of an increase in the initial concentration of sodium chloride is to increase the yield because a high concentration of Cl' ions reduces the discharge of ClO' ions. A very high yield results if the solution is kept saturated throughout the course of the electrolysis. These are shown in Table III.

Table IV records data for the variation of current densities. Increase of the anodic current density increases the yield. This is probably due to the increased oxygen overvoltage and the consequent decrease in the amount of OH' and ClO' ions discharged.

For the prevention of cathodic reduction, it is necessary to add some foreign substance. Potassium dichromate was very early recognised to be effective in this respect and it has been hitherto the most useful *addition agent*. Though it acts catalytically, fairly large quantities are required. It is supposed to form a film of chromium chromate which prevents the contact between the nascent hydrogen and the hypochlorite and chlorate. For example Muller (*Z. Elektrochem.*, 1899, 5, 469; 1901, 7, 398; 1902, 8, 109) showed that no prevention of reduction takes place at a mercury cathode where no coherent film could be formed. Table V shows that substances which are capable of forming an insoluble film round the cathode such as the alkaline and rare-earth elements, generally show a high yield. Manganese, iron and titanium are marked by the fact that their salts reduce the yield considerably. This is probably due to the fact that their salts get easily oxidised at the anode and subsequently reduced at the cathode and thus consume much of the current used.

When the cell is exposed to sunlight neither chlorate nor hypochlorite is found amongst the end products. Perhaps this is due to the fact that the hypochlorous acid is decomposed on exposure to sunlight giving off oxygen and chlorine.



That means, it is necessary to avoid sunlight in chlorate cells. When alternating current is substituted for direct current, no chlorate is formed. The platinum dissolves and gets plated out in the black form. It may be that platinum which is ordinarily '*passive*' gets charged during the transient

cathodic component with hydrogen and loses its passivity and so it dissolves during the next anodic component of the current (Margules, *Ann. Phys.*, 1898, **65**, 629; **66**, 540). This dissolved platinum gets plated out as platinum black during the cathodic half if in the mean while it has not entered into a complex. Moreover, A. C. reduces the overvoltage to a very low value (Reitlinger, *Z. Elektrochem.*, 1914, **20**, 261; Grube and Dulk, *ibid.*, 1918, **24**, 237) and so there is nothing to prevent the discharge of OH' ions in preference to Cl' ions. Since the solution is acidic OH' ions are practically absent; so some Cl' ions may also be discharged. The liberated chlorine will not escape until enough of it has accumulated to form bubbles and escape. But before this takes place the current gets reversed and the chlorine is ionised either cathodically or by reaction with the hydrogen liberated in an active state. So whether Cl' ions are discharged or not no chlorate will be formed.

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Received May 26, 1941.

KINETICS OF HYDROGENATION OF OILS IN A CONTINUOUS PROCESS.

BY R. V. JOGLEKAR AND S. K. K. JATKAR.

The corrected velocity coefficients (k') have been calculated for the hydrogenation of safflower, sesame, cottonseed and groundnut oils in a continuous process. The values 2 and 4 obtained for the exponent n in the equation.

$$k = k'R \frac{x}{n}$$

have been shown to be due to the activated absorption of olein and linolein respectively. The heats of activation calculated for oils containing different percentages of olein and linolein have shown that the heats of activation are about 2K cal. and 8K cal. for olein and linolein respectively.

Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, **96A**, 137) found that the rate of hydrogenation in a batch process is a linear function of time. Similar view is held by Richardson and co-workers (*Ind. Eng. Chem.*, 1924, **16**, 519). Thomas (*J. Soc. Chem. Ind.*, 1920, **39**, 107) found that the hydrogenation of olive oil by batch process is of monomolecular type. Armstrong and Hilditch (*Proc. Roy. Soc.*, 1920, **98A**, 27) explained the gradually decreasing rates observed by Thomas to the use of a closed system and the consequent accumulation of gaseous impurities which acted as poisons. Thomas found an increase of 2.8 times in the rate of reaction for a 60° rise in temperature.

Lush (*J. Soc. Chem. Ind.*, 1924, **44**, 1297) from his study of the hydrogenation of cottonseed oil by the continuous method has shown the absorption of hydrogen to be independent of the flow of oil within certain limits. Athavale and Jatkar (*J. Indian Inst. Sci.*, 1939, **21A**, 321) have made a systematic study of the continuous method of hydrogenation and followed the kinetics of reaction by the space-time yields, assuming that the reaction proceeds in a logarithmic manner along the length of the tube; the percentage conversion in one passage over the catalyst represented an integrated reaction over the whole length of the tube. The formulae used for calculating velocity coefficients was of the first order,

$$k = 2.3 R \log \frac{a}{a-x}$$

where R is the rate of the oil flowing over the catalyst and k is the apparent velocity coefficient. They obtained concordant values at all rates,

in the case of nickel wire catalyst at 140°, 160°, and 180°. The nickel carbonate-kieselguhr catalyst gave varying values for the velocity coefficients in the case of hydrogenation of groundnut, cottonseed and olive oils.

The velocity coefficients calculated from the unimolecular formula is only a measure of the association between the unsaturated compound and the catalyst at a particular rate in unit length of the catalyst. From the variation of the values of k , it appeared that the association between the unsaturated compound and the catalyst is influenced by rate. The variation in the values of k can be expressed by

$$k = k' R^{\frac{1}{n}}$$

where k' and n are positive constants.

Athavale and Jatkars (*loc. cit.*) obtained concordant values for k' in the case of hydrogenation of groundnut, cottonseed and olive oils by nickel carbonate-kieselguhr catalysts. n has been shown by them to be a function of temperature. The present work is an extension of the study of the kinetics of hydrogenation of oils in a continuous process with reference to safflower, sesame, cottonseed and groundnut oils.

EXPERIMENTAL.

The apparatus used was the same as described by Athavale and Jatkars (*loc. cit.*). 20% Nickel carbonate-kieselguhr catalyst was used.

The Velocity Coefficients.

The corrected velocity coefficients for safflower, sesame, cottonseed and groundnut oils, obtained by using the formula $k = k' (r)^{\frac{1}{n}}$ are given in Tables I and II.

TABLE I.

Rate.	Vel. coeff. of safflower oil at					Vel. coeff. of sesame oil at				
	100°.	120°.	140°.	160°.	180°.	100°.	120°.	140°.	160°.	180°.
40	1.09	4.19	2.83	7.67	5.37	2.03	0.47	2.62	1.41	8.27
60	1.03	4.00	2.99	7.48	5.71	2.16	0.43	2.85	1.35	8.10
80	1.10	4.30	3.01	7.47	5.56	2.13	0.43	2.88	1.39	8.46
100	1.08	4.26	2.80	7.36	5.56	2.12	(0.33)	(2.46)	1.31	8.35
Mean	1.05	4.19	2.91	7.50	5.55	2.11	0.44	2.78	1.36	8.30
"	2	3.8	2.3	4.4	2	2.6	1	1.8	1.4	3

TABLE II.

Rate.	Vel. coeff. of cottonseed oil at			Vel. coeff. of groundnut oil at		
	140°.	160°.	180°.	100°.	140°.	180°.
40	(1'82)	9'50	13'6	2'97	4'07	6'91
60	2'23	9'27	(14'6)	2'66	4'17	6'77
80	2'28	9'31	13'7	2'63	4'02	6'88
100	2'17	9'51	13'6	2'61	3'88	6'73
Mean	2'22	9'39	13'65	2'72	4'01	6'82
<i>n</i>	2	4	4	2	2	2

For safflower and sesame oils the apparent velocity coefficients k increase steadily with increasing temperature showing a maximum and a minimum near about 140° and 160° respectively. The maxima and minima are more predominant with faster rates which is in accordance with results obtained by Athavale and Jatkar for groundnut oil (*loc. cit.*) who attributed the peaks in the k -temperature curves to the faster velocity of the hydrogenation of linolein.

The study of the selectivity of hydrogenation by the authors (Joglekar and Jatkar, *J. Indian Inst. Sci.*, 1941, **23A**, 139) has shown that for sesame oil the reaction, olein-stearin proceeds best at 140°. This reaction is less pronounced in the case of safflower oil which has a very high content of linolein.

At 160° for safflower, sesame and cottonseed oils, it has been observed by us (*loc. cit.*) that linolein-stearin reaction takes place exclusively.

The n obtained for groundnut oil is 2 which confirms the value obtained by Athavale and Jatkar. In the case of oils containing higher proportion of linolein ($n=4$) at higher temperatures at which preferential hydrogenation of linolein takes place.

The Apparent Heats of Activation.

The apparent heats of activation E are calculated from the corrected velocity coefficients k' for 20% nickel catalyst at 150°.

TABLE V.

Oil	... Groundnut.	Sesame.	Safflower.	Cottonseed.
<i>E</i>	... 2'1	2'5	7 2	11'1

The lower heat of activation for the hydrogenation of olein than that observed for ethylene and other ethylenic compounds (which is about 10 K cal.) is due to the higher activity of the catalyst. The increased heat of activation for oils containing linolein is obviously accounted for on the basis of increased energy required for activation of two double bonds.

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Received October 24, 1941.

STUDIES IN THE SUBSTITUTED SUCCINIC ACIDS. PART I.

BY RAFAT HUSAIN SIDDIQUI AND SALAH-UD-DIN.

o-Chloro, *o*- and *p*-methoxyphenyl and phenylsuccinic acids and their derivatives have been obtained.

Phenyl and substituted phenylsuccinic acids were required for an investigation but as one of us (S) left the University the work had to be stopped and consequently we publish the results so far achieved. As a result of this investigation *o*-chloro-, *o*- and *p*-methoxyphenyl and phenylsuccinic acids and their derivatives have been obtained by the method of Lapworth and Wikas (*J. Chem. Soc.*, 1917, 111, 796). It consists in condensing the aldehyde and ethyl cyanoacetate in the presence of piperidine when arylidene cyanoacetate results. This on addition of hydrogen cyanide yields a product which on hydrolysis with boiling hydrochloric acid gives the desired succinic acid. It has been incidentally noticed that the arylidene cyanoacetate on addition of hydrogen cyanide in every case gives a crystalline product but its nitrogen value is much too high for $\alpha\beta$ -dicyano- β -aryl propionate and it is hoped that this work will be taken up again.

EXPERIMENTAL.

Commercial *o*-toluidine was freed from the *para* isomer by converting it into insoluble *o*-toluidine hydroferrocyanide by bringing together aqueous solutions of the hydrochloride of the base and sodium ferrocyanide. On decomposing the salt with sodium hydroxide the base distilled at 198°, acetyl derivative, m.p. 110°. The pure base (as hydrochloride) was diazotised at -5° and on adding freshly reduced copper powder the mixture was warmed at 60° to decompose the diazonium compound when the *o*-chlorotoluene separated and distilled at 156°. For the preparation of *o*-chlorobenzaldehyde from *o*-chlorotoluene, oxidation with chromium oxychloride in carbon bisulphide (b.p. 205-10°, *J. Chem. Soc.*, 1888, 53, 803), or chloroform solution (*ibid.*, 1907, 91, 261), was used and the aldehyde was obtained as a semi-solid mass, b.p. 210-14°, but when the aldehyde was prepared by converting *o*-chlorotoluene into *o*-chlorobenzal chloride and hydrolysing the latter with either oxalic or sulphuric acid, it distilled at 210-14° but soon turned into a solid, m.p. 28°, semicarbazone, m.p. 225°. The aldehyde on keeping for a fortnight melted at 54° and after three months had m.p. 125° and it continued to emit aldehydic smell. In the present investigation freshly distilled aldehyde was used,

*Ethyl α -cyano- β -(*o*-chlorophenyl)-acrylate.*—A mixture of freshly distilled *o*-chlorobenzaldehyde (40 g.), ethyl cyanoacetate (35 g.) and piperidine (2 c.c.) was allowed to stand for 12 hours. The ester separated in needles, m.p. 225°. It was filtered at the pump and washed with a little alcohol. It is soluble in acetone, chloroform and difficultly so in alcohol, yield 51 g.

Addition of Hydrogen Cyanide to the above Ester.—A solution of the ester (48 g.) and potassium cyanide (14 g. in 14 c.c. of water) in alcohol (300 c.c.) was allowed to stand for 72 hours. On removal of the solvent a viscous oil separated and no attempt was made to obtain it in the crystalline form.

o-Chlorophenylsuccinic Acid.—The above oily compound (55 g.) was hydrolysed by boiling with concentrated hydrochloric acid (50 c.c.) and water (50 c.c.). On cooling, *o*-chlorophenylsuccinic acid separated in needles, m.p. 155°; recrystallised from ether-petroleum ether mixture, m.p. 177°. It is soluble in ether, acetone, ethyl acetate, alcohol and hot water and insoluble in chloroform, benzene and petroleum ether. (Found in substance dried at 100° in *vacuo*: C, 52.57; H, 4.08; Cl, 15.08. $C_{10}H_7O_4Cl$ requires C, 52.5; H, 3.9; Cl, 15.6 per cent).

o-Chlorophenylsuccinic Anhydride.—A mixture of *o*-chlorophenylsuccinic acid and acetic anhydride was kept simmering for 5 hours and on removal of acetic anhydride in *vacuo* the residue crystallised from chloroform-petroleum ether mixture, m.p. 119–20°.

Monoanilide of o-Chlorophenylsuccinic Acid.—*o*-Chlorophenylsuccinic anhydride (0.1 g.) and an equal proportion of aniline were brought together in benzene and from the solution on warming for a minute or two the anilide separated as snow-white needles, m.p. 168°. (Found in substance dried at 100° in *vacuo*: N, 5.84. $C_{18}H_{13}O_3N$ requires N, 5.2 per cent).

*Ethyl α -cyano- β -(*p*-methoxyphenyl) acrylate* was obtained from anisaldehyde (110 g.), ethyl cyanoacetate (90 g.) and piperidine (2 c.c.) as needles, m.p. 84°, yield 158 g. It is soluble in chloroform, ethyl acetate, benzene, ether, acetone and hot water, insoluble in petroleum ether and difficultly soluble in alcohol. (Found in substance dried in *vacuo*: C, 67.22; H, 5.82; N, 6.36. $C_{15}H_{13}O_3N$ requires C, 67.5; H, 5.6; N, 6.1 per cent).

Addition of Hydrogen Cyanide to the Above.—A mixture of the above acrylate (150 g.), potassium cyanide (30 g. in 40 c.c. of water) and alcohol (1500 c.c.) was kept at room temperature for 48 hours. Three quarters of the solvent were distilled and the residue on cooling at 0° separated in light violet wooly needles. It was recrystallised from dilute alcohol, m.p. 73°. The nitrogen value does not agree with $\alpha\beta$ -dicyano- β -(*p*-methoxyphenyl)-

propionate. (Found in substance dried over P_2O_5 in *vacuo*: N, 15.98. $C_{13}H_{15}O_5N_2$ requires N, 11.3 per cent).

p-Methoxyphenylsuccinic Acid.—The above ester (130 g.) was hydrolysed with concentrated hydrochloric acid (200 c.c.) and water (150 c.c.) under reflux for 4 hours. The oil which separated on cooling deposited needles (105 g.). From acetone white needles, m.p. 206° , were obtained. (Found in material dried at 100° in *vacuo*: C, 59.00; H, 5.56. Calc. for $C_{11}H_{12}O_5$: C, 58.9; H, 5.4 per cent).

The *anhydride* was prepared by the usual method and crystallised from chloroform-petroleum ether in needles, m.p. $92-93^\circ$. *Monoanilide*, m.p. 122° ; *p-methoxyphenylsuccinil* was obtained when the monoanilide was heated above its m.p. in a sulphuric acid bath and crystallised from benzene. m.p. $140-42^\circ$. *Mono-o-toluidide*, m.p. 156° (white needles); *o-tolil*, m.p. 170° ; *mono-p-toluidide*, m.p. 176° ; *p-tolil*, m.p. $140-42^\circ$.

Ethyl α -cyano- β -(o-methoxyphenyl)-acrylate was obtained as light yellow needles, m.p. 77° ; hydrogen cyanide addition product of the acrylate was obtained as colourless needles from alcohol, m.p. 85° . (Found in substance dried over P_2O_5 in *vacuo*: N, 16.52. $C_{13}H_{15}O_5N_2$ requires N, 11.3 per cent).

o-Methoxyphenylsuccinic Acid.—The above hydrogen cyanide addition product of the acrylate on hydrolysis with concentrated hydrochloric acid gave *o*-methoxyphenylsuccinic acid (white needles), m.p. 182° .

Ethyl α -cyano- β -phenylacrylate separated as needles from petrol, m.p. 54° . The hydrogen cyanide addition product of the acrylate was obtained as needles, m.p. 69° (Ethyl $\alpha\beta$ -dicyano- β -phenylpropionate, prepared by a different method, melts at 64° , *J. Chem. Soc.*, 1908, 93, 1471). The nitrogen value of this is also too high. (Found in substance dried over P_2O_5 : N, 19.04. $C_{12}H_{13}O_5N_2$ requires N, 13.0 per cent). The mother-liquor from the hydrogen cyanide addition product in every case gave the same acid as the crystalline derivative. The hydrogen cyanide addition product on hydrolysis by the usual method gave phenylsuccinic acid, which was obtained as colourless needles from ether, m.p. 172° .

The authors wish to express their thanks to the Honorary Secretary, Indian Chemical Society, for some of the nitrogen analyses. Other micro analyses were done by Dr. Ing. A. Schoeller, Berlin.

THE CHEMICAL LABORATORIES,
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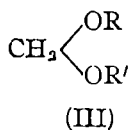
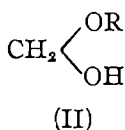
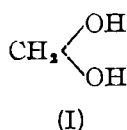
Received November 4, 1941.

A METHOD OF PREPARING MONO-ETHERS OF METHYLENEGLYCOL.

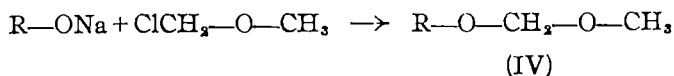
BY M. L. GUPTA, R. KAUSHAL AND S. S. DESHPANDE.

By the action of chloromethyl acetate on sodium derivative of an alcohol, an ether acetate of methyleneglycol results, from which on alkali hydrolysis the corresponding mono-ether is obtained. The preparation of the monobenzyl ether is described.

Methyleneglycol (I) is not known. Its mono-ethers (II) are not described in literature. Its diethers (III) are the acetals of formaldehyde, and, when symmetrical ($R=R'$), are obtained by the usual process of con-

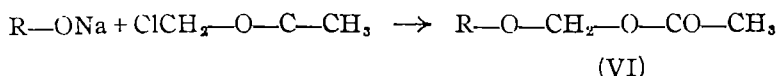


densing the aldehyde with alcohols. Among its unsymmetrical diethers the better known are the methyl ethers which are obtained by condensing monochloromethyl ether with sodium derivative of an alcohol.



The mono-ethers (II) cannot be prepared by the action of dilute aqueous alkali on a halogen ether such as the iodoether $\text{R-O-CH}_2\text{I}$ (V) (which might result from (IV) by fission with HI]. For, as has been shown by Wedekind (*Ber.*, 1901, **34**, 814; 1903, **36**, 1384) the halogen ethers (V) are decomposed by water giving formaldehyde. Thus chloromethyl menthyl ether gives menthol, formaldehyde and hydrochloric acid (*ibid.*, 1903, **34**, 814).

If, however, the sodium derivative of an alcohol is condensed with chloromethyl acetate the resulting compound will be an ether acetate of methyleneglycol.



The ester part of (VI) could be hydrolysed by alkali which will not attack the ether link, and the desired mono-ether of methyleneglycol will result,

This plan worked, and the monobenzyl ether of methyleneglycol (II, $R = C_6H_5-CH_2-$) was prepared in a fairly good yield through the acetate (VI) ($R = C_6H_5-CH_2-$) which in its turn was obtained from sodium derivative of benzyl alcohol and chloromethyl acetate.

Benzyl ether of methyleneglycol is a liquid, somewhat soluble in water. It is characterised by the formation of its phenylurethane, which is readily obtained. Nitric acid oxidises the ether to benzoic acid.

During the course of the work the unsymmetrical methylbenzyl ether of methyleneglycol has been prepared by the method shown for formation of (IV). This compound has not so far been described. In a Zeisel estimation it gives theoretical yield of methyl iodide.

EXPERIMENTAL.

Chloromethyl acetate was prepared by the method of Desende (*Compt. rend.*, 1901, 132, 1568). Acetyl chloride (13 g.) and trioxymethylene (15 g.) were refluxed in presence of zinc chloride and the product of reaction was distilled at reduced pressure when 11 g. of a liquid boiling at $58^{\circ}-62^{\circ}/29\text{cm.}$ was obtained.

The Acetate of Methyleneglycol monobenzyl Ether (VI, $R = C_6H_5-CH_2-$).—Benzyl alcohol (8.5 g.) was dissolved in dry benzene and equivalent amount of sodium (in the form of wire) was added. On refluxing for 3 hours on a water-bath, a white suspension of the sodium derivative of benzyl alcohol was obtained. Chloromethyl acetate (11 g.) was then gradually added and the whole refluxed on a water-bath for 4 hours. The sodium chloride formed was filtered off and benzene distilled from the filtrate. The remaining liquid was then distilled under reduced pressure when a fraction boiling between $152^{\circ}-155^{\circ}/29\text{ mm.}$ was obtained, yield 2.5 g. (Found: C, 66.2; H, 6.2. $C_{10}H_{12}O_3$ requires C, 66.6; H, 6.7 per cent).

The acetate is a thin liquid with a somewhat penetrating odour resembling that of formalin.

Methyleneglycol monobenzyl Ether (II, $R = C_6H_5-CH_2-$).—The acetate (2 g.) was hydrolysed with potassium hydroxide (1 g. dissolved in 10 c.c. of 90% alcohol) by refluxing on a water-bath for 3 hours. The reaction mixture was poured into water and extracted with ether. On drying and removing the solvent the remaining liquid was distilled under reduced pressure, when the monobenzyl ether passed between $75^{\circ}-77^{\circ}/4\text{ mm.}$ (Found: C, 69.3; H, 7.3. $C_8H_{10}O_2$ requires C, 69.6; H, 7.3 per cent).

The monobenzyl ether is a thin liquid, somewhat soluble in water and has a faint sweet odour. With phenylisocyanate it readily gave the phenyl-

urethane, which crystallised from alcohol, m.p. 75° . (Found : N, 5.45. $C_{15}H_{15}O_4N$ requires N, 5.15 per cent).

With concentrated nitric acid and a drop of sulphuric acid the monobenzyl ether was oxidised to benzoic acid which was identified by its melting point and its equivalent weight.

Methyleneglycol methylbenzyl Ether (IV, $R = C_6H_5-CH_2-$).—Sodium derivative of benzyl alcohol, obtained from 10.8 g. of the alcohol and equivalent amount of sodium, was suspended in dry benzene and monochloromethyl ether (12 g.) was added, and the whole was refluxed until the reaction mixture was neutral (3 hours). On filtering and distilling off the solvent the remaining liquid was distilled under reduced pressure when two fractions were obtained :

- (i) B.p. $84^{\circ}-87^{\circ}/8$ mm. (3 g.)
- (ii) B.p. $165^{\circ}-67^{\circ}/8$ mm. (3 g.)

Fraction (ii) was not investigated. Fraction (i) was analysed. (Found : C, 70.3 ; H, 7.3 ; OMe, 19.6. $C_9H_{12}O_2$ requires C, 71.0 ; H, 7.9 ; OMe, 20.4 per cent).

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Received October 31, 1941.

CHEMICAL EXAMINATION OF *THALICTRUM FOLIOLOSUM* DC. ISOLATION AND CHARACTERISATION OF A NEW ALKALOID, THALICTRINE.

BY SHIAM KISHORE VASHISTHA AND SALIMUZZAMAN SIDDIQI.

Berberine and a new quaternary ammonium base, thalictrine, have been obtained from *Thalictrum foliolosum* DC. Thalictrine has been characterised by the preparation of several derivatives.

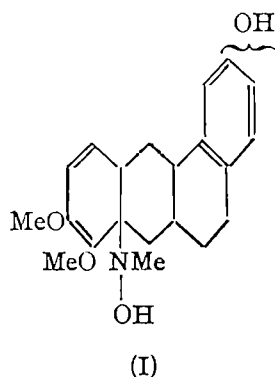
Thalictrum foliolosum DC. (N.O. *Renunculaceae*; Hindi, Pilijari, Mamiri) occurs in temperate Himalaya and Khasia hills. Its rhizome is considered to be a tonic and laxative and a good substitute for Rhubarb, but it is chiefly used in indigenous medicine as a cheap but valuable substitute for mamira (*Coptis teeta*) in the preparation of collyriums for ophthalmic troubles. Both *Coptis teeta* (Hooper, *Pharm. J.* 1912, **34**, iv, 482) and *Thalictrum foliolosum* (Dymock, "Pharmacographia Indica", Vol I, p. 33) are reported to contain large quantities of water-soluble salts of berberine, but as berberine alone could not reasonably account for the beneficial properties attributed to these two drugs, we thought it of interest to make a comparative study of their chemical constituents. The present paper deals with the chemical examination of *Thalictrum foliolosum*, as a result of which the following products have been obtained :

1. Berberine (yield, ca. 0.24% on the weight of the dry powdered drug).
2. A new quaternary ammonium base, $C_{20}H_{27}O_4N$, m.p. 208° , $[\alpha]_D^{25} = +308^\circ$ in 1% aqueous solution (yield, 0.2%), which has been named by us as Thalictrine.

The method of separation of the alkaloids was based on the difference in the solubility of their iodides. Thus, while berberine iodide is insoluble in water, and sparingly soluble in methanol, thalictrine iodide is readily soluble in water and is isolated through its insoluble bismuth double salt. The mother-liquors of berberine iodide (m.p. 260°) gives a yellow coloured iodide melting at 206° . This indicates the presence of yet another base but the quantity of the lower melting iodide is not sufficient for further investigation.

Thalictrine crystallises from dilute methanol with 3 molecules of water of crystallisation which it completely loses *in vacuo* at 100° . Prolonged heating of the dehydrated base at 140° in an atmosphere of hydrogen

darkens the colour but causes no further decrease in its weight. Its quaternary character, established through the analysis of its salts and its inability to add methyl iodide, is not affected by heating under conditions mentioned above. Thalictrine contains two methoxyls, one *N*-methyl and two olefine double bonds, deduced from its behaviour towards bromine in the cold. These findings suggested that thalictrine might be derived from a hexahydro product of berberine, in which the nitrogen ring is reduced. The presence of a phenolic hydroxyl is indicated in thalictrine through intense brown-violet colouration with ferric chloride and the absence of methylene oxide and methyl groups is shown by a negative phloroglucinol-sulphuric acid reaction and a negative side-chain methyl value. In view of all these facts thalictrine has been tentatively assigned the structure (I) to show its probable genetic connection with berberine, the main alkaloid of this plant.



In the course of this investigation it has also been noted that the rhizome of *thalictrum foliolosum* is appreciably hygroscopic in character and does not stock well. After about six months' keeping of the same sample, the yield of crystalline berberine hydro-iodide was reduced to nearly a quarter, while thalictrine could be obtained only in traces. An examination of the pharmacological action of thalictrine is projected.

E X P E R I M E N T A L.

A fresh supply of the drug was obtained from the Himalayan Drug Company, Dehra Dun. It was identified by Messrs. N. L. Bor and C. E. Parkinson, Botanists, Forest Research Institute, Dehra Dun, and also by the Superintendent, Royal Botanic Garden, Sibpur, Calcutta, to whom the authors' sincerest thanks are due.

A fat-free sample of the drug powder gave on complete ignition 5% of ash, which showed the presence of iron, calcium, magnesium, potassium, phosphate, carbonate, and traces of sulphate and halogen.

After a series of preliminary experiments 2 kg. of well-powdered rhizome were percolated 3 times in the cold with methanol. The combined percolates (about 4 litres) were concentrated below 45° in *vacuo* to a soft extract, which was of a yellowish brown colour. This was taken up in about 500 c.c. of water and shaken out with ether (1 litre) to separate the fatty fraction.

Separation of Berberine and Thalictrine.

The yellowish brown aqueous solution from above was treated with potassium iodide, and the heavy yellowish precipitate was filtered and well washed with water. The precipitate weighed 12 g. after drying on a porous plate. The methanol-insoluble portion of this iodide gave 6 g. of berberine iodide (m.p. 260°) after purification through 10% acetic acid and alcoholic hydrochloric acid.

The combined aqueous filtrate and washings from the original iodide precipitate were treated with an excess of Dragendorff's reagent, and the bisnuth double salt precipitate was sucked and successively washed with water, alcohol and finally some ether. The dry powder was then suspended in 50% dilute methanol and treated with an excess of freshly precipitated silver hydroxide, filtered and repeatedly washed with hot dilute methanol and finally with water. The black residue was rejected and the methanol-water extracts were carefully concentrated till nearly free from the solvent. The pasty concentrate was then extracted with methanol and the methanol solution treated with ether and a little petroleum ether which removed dark reddish impurities, leaving a nearly colourless solution from which thalictrine crystallised out in the cold as stars of needles. After repeated crystallisations from methanol the base finally melted at 208°, subsequent recrystallisation leaving the m.p. unaltered (yield, 4 g.).

The dark coloured methanol extract (125 c.c.) from the total iodide precipitate, obtained at the outset, was treated with ether and petroleum ether. The reddish yellow filtrate from the dark brown oily precipitate gave a yellow coloured iodide, which melted at 206° (as against berberine iodide melting at 260° and thalictrine iodide melting at 265°), was insoluble in water and thus appeared to be the iodide of a base different from both berberine and thalictrine. The rest of the methanol extract as also the acetic acid and the alcoholic hydrochloric acid extracts from the initial iodide precipitate appeared to consist of mixtures of the iodides of the three bases and were not pursued further.

Characterisation of Thalictrine.

Thalictrine, $C_{20}H_{27}O_4N$, $C_{17}H_{16}(OH)(OMe)_2$, $NMe(OH)$, crystallises from dilute alcohol with three molecules of water of crystallisation, m.p. 208° . On drying to constant weight in *vacuo* at 100° over P_2O_5 the air-dried crystals lost 13.6% of their weight. $C_{20}H_{27}O_4N, 3H_2O$ requires H_2O , 13.5%. (Found in the air-dried sample: C, 60.8; H, 8.2, $C_{20}H_{27}O_4N, 3H_2O$ requires C, 60.2; H, 8.3 per cent). As obtained after drying to constant weight at 100° , thalictrine forms a white crystalline powder which begins to shrink with darkening from 190° onwards, melts down giving a meniscus at 223° and decomposes at $224-25^\circ$. The dehydrated base suffers no further loss in weight when kept at 140° for 3 hours in an atmosphere of hydrogen. It is easily soluble in water and alcohol but sparingly so in dry benzene, acetone, ether and petroleum ether and shows $[\alpha]_D^{24} = +370^\circ$, as against $[\alpha]_D^{24} = +308^\circ$ for thalictrine containing 3 molecules of water of crystallisation. The free base deteriorates on stocking and absorbs atmospheric carbon dioxide. (Found in dehydrated base: C, 69.8, 70.11; H, 7.01, 7.7; N, 4.1, 4.5. $C_{20}H_{27}O_4N$ requires C, 69.6; H, 7.8, N, 4.1 per cent). Thalictrine gave a negative value in the $CH_3(C)$ determination.

Determination of OMe and NMe (Zeisel, Herzig and Meyer's methods) showed the presence of 2(OMe) and 1(NMe). [Found in dehydrated base; OMe, 18.06; NMe, 5.16. $C_{20}H_{27}O_4N$ requires (for 2OMe) OMe, 18.02 and (for 1 NMe) Me, 4.4 per cent].

Thalictrine decolourises acidified potassium permanganate solution without showing any fluorescence and does not form an insoluble compound with acetone. In concentrated sulphuric acid the base dissolves with a pinkish colour which changes through reddish violet to bluish violet. The blue tinge deepens on standing. Drops of water lighten the colour and further dilution gives a reddish yellow solution. In concentrated nitric acid it dissolves with an orange-red colour which fades down to straw yellow on warming. Dilute nitric acid dissolves it with a deep red colour. Chlorine water when added to an aqueous solution of its hydrochloride gives an immediate deep red colouration which lightens on standing.

Thalictrine chloride came out on adding ether and petroleum ether to a concentrated solution of the base in alcoholic hydrochloric acid as an oil, which when washed repeatedly with ether and evacuated, formed a white hygroscopic powder. It softens from 161° onwards and froths up at $163-65^\circ$. (Found after drying to constant weight at ordinary temperature: Cl, 10.2. $C_{20}H_{26}O_3N$ Cl requires Cl, 9.8 per cent).

Thalictrine chloroplatinate was obtained by adding a 5% solution of platinic chloride to a solution of the chloride as a pale yellow precipitate which after washing and drying in *vacuo* became nearly colourless. It begins to darken from 215° onwards, swells at 231° and decomposes at $233\text{--}34^{\circ}$. [Found : Pt, 17.3. $(C_{22}H_{20}O_5N\ Cl)_2$, $PtCl_4$ requires Pt, 18.3 per cent].

Thalictrine iodide was prepared by bringing together the components in absolute alcohol medium. Crystallised from a mixture of alcohol, acetone and ether it was obtained as a light cream-coloured powder, easily soluble in water and alcohol, m.p. 265° (decomp.). (Found after drying to constant weight at 100° . I, 27.8. $C_{22}H_{20}O_5NI$ requires I, 27.9 per cent).

Thalictrine picrate was obtained by adding aqueous picric acid to an aqueous solution of the base. On recrystallisation from methanol it formed aggregates of stout, spike-shaped, bright yellow needles, fairly soluble in hot alcohol; sparingly so in water and melting at $207\text{--}8^{\circ}$.

Tetrabromothalictrine acetate.—To the base (0.15 g.) in glacial acetic acid (5 c.c.) was slowly added 1% solution of bromine in the same solvent (equiv. to 4 Br) with ice-cooling. In the beginning every fresh addition produced a yellow thread-like precipitate which dissolved on shaking, giving a yellow tinge to the solution, but on further addition a permanent granular yellow precipitate settled down. This was filtered, well washed with ether and dried on a porous plate. From the ethereal washings a further quantity of the bromo product crystallised out in stars of orange-coloured needles. The bromo derivative is soluble in alcohol and water, sparingly soluble in chloroform, ethyl acetate and glacial acetic acid, and insoluble in ether. It begins to blacken and shrink from 200° onwards and decomposes with frothing at $248\text{--}50^{\circ}$. (Found after drying to constant weight at 100° over P_2O_5 : Br, 46.4. $C_{22}H_{20}O_5NBr_4$ requires Br, 45.3 per cent).

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Received September 22, 1941

VARIATIONS IN THE ELECTROCHEMICAL PROPERTIES OF HYDROGEN CLAY SOLS WITH TEMPERATURE*

BY B. CHATTERJEE† AND A. SEN.

In a previous note (Mukherjee, Chatterjee and Sen, *J. Indian Chem. Soc.*, 1941, 18, 283) it has been shown that the free and total acids as also the degree of dissociation of silicic acid and hydrogen bentonite sols do not materially change with temperature between 1° and 50°. Variations with temperature of the free and total acids, degree of dissociation and the forms of the titration curves of hydrogen clay sol H, prepared from the entire clay fraction of a neutral calcareous soil from Government Seed Farm, Kalyanpore (U.P.) collected at a depth of 0 to 6 inches, are given in this note (Table I).

TABLE I.

Colloid content=11.0 g. per litre.

p_H .			Free acidity $\times 10^5 N.$			Total acidity‡ $\times 10^5 N.$			$\alpha\%$			p_H at inflexion		
1°	35°	50°	1°	35°	50°	1°	35°	50°	1°	35°	50°	1°	35°	50°
5.07	4.84	4.61	0.96	1.5	2.5	286	286	286	0.33	0.52	0.87	9.05	8.25	7.75
4.97	4.79	4.60												

Unlike hydrosols of silicic acid and hydrogen bentonite, hydrogen clay sols show an increase of free acidity with a rise of temperature; but in agreement with the other sols they (sol H. fig. 1) give the same total acidity at different temperatures. The inflexion points, however, become displaced to higher p_H values with decreasing temperatures. The degree

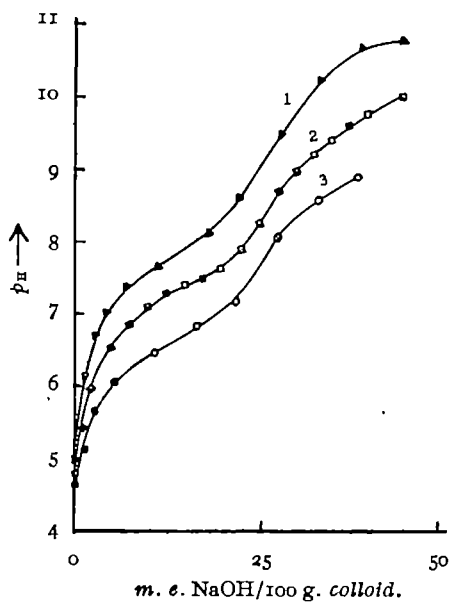
* The results have been taken from the published annual report for 1939-40 on the working of a 'Scheme of Research into the Properties of Colloid Soil Constituents' financed by the Imperial Council of Agricultural Research, India and directed by Prof. J. N. Mukherjee, D.Sc.

† Assistant Soil Chemist under the above scheme.

‡ Reproducible within $\pm 2\%$.

of dissociation, ratio of free to total acids, increases with temperature. Further work on this point with hydrogen clay sols is in progress.

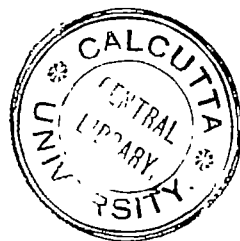
Hydrogen clay sol.



Curves 1—3 refer respectively to titration at 1°, 35° and 50°.

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Received October 31, 1941.



Journal of the Indian Chemical Society
Vol. XVIII, 1941.

INDEX OF AUTHORS

	PAGE
ACHARYA, Harendra Kumar. —Properties of activated sugar charcoal coated with various organic substances. Part III. Catalytic decomposition of hydrogen peroxide	15
AHLUWALIA, Ganga Singh. —See Sardar MOHAMMAD.	
AHLUWALIA, Gurcharan Singh. —See H. D. SURI.	
AHMAD Z. —See S. SIDDIQUI.	
ALIMCHANDANI, R. L. —See D. R. KULKARNI.	
BADAR-UD-DIN. —See P. L. KAPUR.	
BAGCHI, Phanindra Nath. —See P. C. MITTER.	
BAHL, R. K. and Manohar LAL. —The action of chlorine on the hydroxides of iron and chromium in the presence of iodine	359
BAHL, R.K. and Surjit SINGH. —The ternary system. Ammonium nitrate-ammonium-sulphate water at 25°	307
BAHL, R. K., Surjit SINGH and Narindra K. BALI —Estimation of iodine in periodates	58
BALI, Narendra K. —See R. K. BAHL.	
BASU, U. P. and S. J. DAS-GUPTA —A note on certain heterocyclic sulphonamides	167
BHATNAGAR, Anand Swaroop. —See S. S. BHATNAGAR.	
BHATNAGAR, S. S., P. L. KAPUR, Anand Swaroop BHATNAGAR and Brahm PRAKASH. —Magnetism and catalysis. Part IV. Catalysis of the reaction between ammonium oxalate and mercuric chloride by ferric ions	371
BHATNAGAR, S. S., P. L. KAPUR, Anand Swaroop BHATNAGAR and M. A. QAYYUM. —Magnetism and catalysis. Part V. A magnetic study of the catalytic decomposition of potassium chlorate by cobaltous oxide and ferromagnetic variety of ferric oxide	391
BHATNAGAR, S. S., Brahm PRAKASH and Mohammed Abdul QAYYUM. —The magnetic susceptibilities of metallic oxides and their molecular structures with special reference to those of cobalt	540
BHATNAGAR, S. S. and Mahendra SARUP. —Adsorptive properties of synthetic resins. Part V.	447

BHATNAGAR, S. S., N. A. VAJNİK, P. L. KAPUR and Anand Swaroop	
BHATNAGAR.—Magnetism and catalysis. Part III. Chlorination of chloroform to carbon tetrachloride	... 350
BHATTACHARJEE, Sasanka Chandra.—See S. S. GUHA-SIRCAR.	
BHATTACHARYA, Abani K.—Composition of Prussian and Turnbull's blues. Part IV. Study of their adsorptive properties	.. 71
—Do. Part V. Role of hydrolysis and their compositions	... 81
—Do. Part VI. Magnetic susceptibility of the compounds	... 85
BHATTACHARYYA, S. K.—Iodination. Part IV. Studies on the photo-iodination of different unsaturated organic compounds in light of different frequencies in non-polar solvents	... 257
—Iodination. Part V. Studies on the photo-iodination of phenylacetylene in light of different frequencies in polar solvent	.. 269
BHATTACHARYYA, S. K. and M. J. RAO—Iodination. Part III. Studies on the iodination of different unsaturated organic compounds in the dark in polar solvents	... 253
—See also J. C. GHOSH.	
BOSE, Amalendu.—See Nripendra Nath CHATTERJEE.	
CHAKRAVARTI, Amritanshu Sekhar and Balbhadra PRASAD.—Apparent molal volumes of electrolyte mixture in aqueous solution	... 239
CHAKRAVARTY, Kshitishranjan.—See Priyadarshan RAY.	
CHATTERJEE, B and A SEN.—Variations in the electrochemical properties of hydrogen clay sols with temperature	... 646
—See also Jnenendra Nath MUKHERJEE.	
CHATTERJEE, D. P.—A note on the separation of silicon and tin in tin-silica mixture, welding brasses and silicon brasses by alkali sulphate	... 591
CHATTERJEE, Nripendra Nath and Amalendu BOSK.—A new synthesis of eudalene	... 196
CHATTERJEE, R.—Oxalenediamidoxime. Part II.	... 19
DAROGA, R. P.—The colorimetric (<i>p</i> -dimethylaminobenzaldehyde-sulphuric acid) method for determining small quantities of atropine	579
DAS-GUPTA, Debabrata and Tejendra Nath GHOSH.—Quinoline derivatives. Part VI	... 120
DAS-GUPTA, J.—Micro-analytical method for the estimation of ferrous and ferric iron in minerals	... 375
—Microchemical investigations on spotted muscovite mica	... 381
DAS-GUPTA, S. J.—Acridine derivatives. Part VI	.. 25
—Do. Part VII. Compounds with mercury, copper and antimony	93
—A new reagent for the estimation of mercury and copper	... 43

—See U. P. BASU.

DESHAPANDE, S. S.—See S. N. JOSHI; also M. L. GUPTA.

DOJA, M. Q.—The sensitisation spectra of certain cyanine dyes derived from α -picoline ... 281

DUNNICLIFF, H. B.—See H. D. SURI.

DUTT, M. M.—See J. C. GHOSH.

DUTT, Nihar Kumar.—See Priyadarajan RAY.

DUTTA, Paresh Chandra.—9-Thiolphenanthrene and some of its derivatives ... 469

DUTTA, Paresh Chandra and Ramani Mohan SINHA.—Azine dyes derived from 9 : 10-phenanthrathioephene-2' : 3'-dione ... 477

DUTTA, Phanindra Chandra.—A new synthesis of cadalene ... 233

GAIND, (Miss) K. N., S. KAPOOR and J. N. RAY.—New methods of synthesis of isoquinoline derivatives ... 213

GAIND, K. N., R. P. SEHGAL and J. N. RAY.—Sulphonamides. Part II. 209

GHOSH, B. N.—On the velocity of hydration and dehydration of nickel sulphate ... 472

GHOSH, J. C., S. K. BHATTACHARYYA, M. M. DUTT and M. J. RAO.—Iodination. Part I. Studies on the equilibrium in systems of iodine and various unsaturated organic compounds in the dark in different non-polar solvents ... 171

—Do. Part II. Studies on the iodination of different unsaturated organic compounds in the dark in different non-polar solvents ... 245

GHOSH, Tejendra Nath.—See Debabrata DAS-GUPTA.

GIRI, K. V.—The influence of vitamin-C on the inactivation of enzymes by ultraviolet light ... 141

—See P. V. KRISHNAMURTHY.

GODBOLE, N. N., B. G. GUNDE and P. D. SRIVASTAVA.—The seed fat of *Buchanania latifolia* ... 557

GOPALARAO, G. and K. S. MURTY.—Photosensitisation of solids. Part II. Photosensitised oxidation of ammonia in aqueous solution with titania as the photosensitiser ... 127

GOPALARAO, G. and Ch. I. VARADANAM.—Do. Part III. Photosensitised oxidation of ammonia in aqueous solution with colloidal titania as the photosensitiser ... 361

—See also T. V. Subba RAO.

GUHA-SIRCAR, S. S. and Sasanka Chandra BHATTACHARJEE.—The use of nitroso derivatives as reagents in inorganic analysis. Part I ... 155

—Do. Part II. ... 161

GUNDE, B. G.—See N. N. GODBOLE.

- GUPTA, Jagannath and Anil Kumar MAJUMDAR.—Raman spectra of substituted sulphuric acids. Part I. ... 457
- GUPTA, M. L., R. KAUSHAL and S. S. DESHAPANDE.—A method of preparing mono-ethers of methyleneglycol ... 638
- GURSAHANI, G. T.—See C. S. NARWANI.
- GWAN, Yeo Sein —A new method of preparation of aceto- and benzonitriles ... 164
- HOON, R. C., J. K. MALHOTRA and Lakshmi Chand JAIN.—The conductometric method of determining the soluble salt content of soils for use in soil survey work ... 103
- JAIN, Kesho Dass and J. B. JHA.—Adsorption of polybasic organic and inorganic acids Discontinuities in adsorption process from solutions of sugar charcoal ... 321
- Adsorption of hydroxybenzenes by sugar charcoal. Discontinuities in the adsorption of phenol, resorcinol and quinol from aqueous solutions ... 535
- JAIN, Kesho Dass and B. L. VAISH.—Reaction between glucose and iodine in alkaline medium. Effect of neutral salts ... 503
- JAIN, Lakshmi Chand.—See R. C. HOON.
- JATKAR, S. K. K —See R. V. JOGLEKAR.
- JHA, J. B.—See Kesho Dass JAIN.
- JOGLEKAR, R. V. and S. K. K. JATKAR.—Kinetics of hydrogenation of oils in a continuous process ... 631
- JOSHI, Bhaskar Govind.—See Dushyant Narasingaśa SOLANKI.
- JOSHI, Shridhar Sarvottam and A. PURUSHOTTAM.—Coagulation of colloids by exposure to high frequency oscillations ... 138
- JOSHI, Siridhar Sarvottam and K. SRINIVASAN —Electrochemical preparation of sodium chlorate from aqueous sodium chloride ... 623
- JOSHI, S. N., R. KAUSHAL and S. S. DESHAPANDE.—Structure of oxymethylene methyl ethyl ketone and of oxymethylene methyl- β -phenyl ethyl ketone ... 479
- KAPOOR, (Miss) S —See K. N. GAIND.
- KAPUR, P. L. and BADAR-UD-DIN.—Estimation of copper in presence of iron ... 585
- KAPUR, P. L.—See S. S. BHATNAGAR.
- KAUSHAL, R.—See S. N. JOSHI; also M. L. GUPTA.
- KRALJ, Hans.—See Ramchandra SAHASRABUDHE.
- KRISHNA, S.—See S. V. PUNTAMBKAR.
- KRISHNAMURTHY, P. V.—Studies in vitamin-C oxidation Part III. The Retardation of Vitamin-C oxidation by Oxalic Acid ... 201

- Complex formation by ascorbic acid with formaldehyde ... 383
- KRISHNAMURTHY, P. V. and K. V. GIRI.—Studies in Vitamin-C oxidation. Part I. Co-existence of oxidising and protective factors in plants for vitamin-C ... 7
- Do. Part II. Influence of various substances occurring in plant and animal tissues on the catalytic oxidation of vitamin-C ... 191
- KULKARNI, D. R., R. L. ALIMCHANDANI and N. M. SHAH.—The condensation of α -substituted acetoacetates with phenols. Part III. The Pechmann condensation of ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate ... 113
- Do. Part IV. The condensation of cresols and other less reactive phenols with ethyl α -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-acetoacetate ... 123
- LAL, Manohar.—See R. K. BAHL.
- MAJUMDAR, Anil Kumar.—Oxanilic acid thioamide as an analytical reagent ... 415
- Quinoline-8-carboxylic acid as an analytical reagent. Part I. ... 419
- See also Jagannath GUPTA.
- MALHOTRA, J. K.—See R. C. HOON.
- MITTER, P. C. and Phanindra Nath BAGCHI.—Studies in long-chain acids. Part III. On *bis-nor*-oleic acid ... 461
- MOHAMMAD, Sardar and Ganga Singh AHLUWALIA.—The action of hydrogen sulphide on permanganates. Part I. Calcium and silver permanganates ... 309
- MONDAL, Kanai Lal.—See Panchanan NEOGI.
- MOOKERJEE, (Miss) Asima.—The alkaloids of *Rauwolfia canescens* Linn. Part I. ... 32
- Do. Part II. ... 485
- MUKHERJEE, Jnanendra Nath, Barodananda CHATTERJEE and Amitabha SEN.—Variations in the electro-chemical properties of silicic acid and hydrogen bentonite sols with temperature ... 283
- MURTY, K. S.—See G. GOPALARAO.
- NARWANI, C. S. and G. T. GURSAHANI.—Base exchange of mercuric ions adsorbed on wool ... 527
- Rhythmic precipitation of silver chloride in gelatin tanned with chromium chloride ... 531
- NEOGI, Panchanan and Kanai Lal MONDAL.—Co-ordinated mercury compounds with ethylene and propylene diamines ... 146
- PANSE, T. B., R. C. SHAH and T. S. WHEELER.—Some new reactions of 1-benzylidene-coumaran-2-ones. Part I ... 453
- PRAKASH, BRAHM.—See S. S. BHATNAGAR.

- PRASAD, Balbhadra.—See Amritanshu Sekhar CHAKRAVARTI.
- PUNTAMBEKAR, S. V. and S. KRISHNA.—The fatty oil from the seeds of *solanum indicum*, Linn. 329
- PURAKAYASTHA, Bhupesh Chandra.—See Priyadarajan RAY.
- PURI, V. S. and S. R. SETH.—The effect of colloids on the electro-deposition of nickel on copper. 465
- PURUSHOTTAM, A.—See Shridhar Sarvottam JOSHI.
- QAYYUM, M. A.—See S. S. BHATTAGAR.
- RAMA CHAR, T. L.—Studies on the photochemical activity of mixtures of vanadic acid and tartaric acid. Part I. Optical properties of mixtures of vanadic acid and tartaric acid. Reduction of these mixtures in light and in the dark 507
- Do. Part II. Photocatalysis by colloidal micelle obtained by the reduction of vanadic acid and tartaric acid. Induced optical activity by circularly polarised light 563
- Do. Part III. Induced circular dichroism in vanadic acid sol. Photoreduction of dichroic sol by tartaric acid in circularly polarised light 605
- RAO, A. L. Sundara.—Studies in hydrogen bond formation. Part I. Amides 337
- RAO, M. J.—See J. C. GHOSH and also S. K. BHATTACHARYYA.
- RAO, M. S. Venkatasubba.—See L. SIBAIYA.
- RAO, P. L. Narasimha.—Chemotherapy of bacterial infections. Part II. Chemistry of some organo-selenium compounds related to sulph-anilamide 401
- Do. Part III. N^1 - β -Phenylethylsulphanilamides 431
- RAO, T. V. Subba. and G. GOPALARAO.—Decomposition of potassium nitrite in sunlight 229
- RAY, J. N.—See K. N. GAIK.
- RAY, Priyadarajan. and Kshitishranjan CHAKRAVARTY.—Complex compounds of biguanide with bivalent metals. Part III. Copper and nickel phenylbiguanides and their different modifications 609
- RAY, Priyadarajan and Nihar Kumar DUTT.—Complex compounds of biguanide with trivalent metals. Part VIII. Resolution of cobaltic trisbiguanide complex into its optically active enantiomerides 239
- RAY, Priyadarajan and Bhupesh Chandra PURAKAYASTHA.—Complex compounds of biguanide with bivalent metals. Part II. Nickel biguanidines 217
- RAY, Priyadarajan and Jaminibhusan ROY-CHOWDHURY.—Biguanide sulphate as a reagent for the estimation of copper 149

- RAY, Priyadarajan, and Sushil Kumar SIDDHANTA.—Complex compounds of biguanide with tervalent metals. Part IX. Action of mercuric chloride and silver nitrate upon chromium and cobaltic bisbiguanidinium hydroxides and the constitution of biguanide metal complexes ... 298
- On the composition and constitution of paramolybdates ... 397
- RAYCHOPHURY, Prodosh Chandra.—Complex chromi-selenates ... 97
- On the study of the dehydration of some pure and mixed chromi-selenic alums and the formation of corresponding complex chromi-selenates ... 277
- Periodates of quadrivalent metals ... 335
- Normal aluminium chromate ... 573
- Periodates of trivalent metals ... 576
- ROY, Amaresh Chandra.—The azo compounds from morphine. Part I ... 29
- ROY, M. B.—A new colorimetric method for the chlorate ion ... 165
- ROY-CHOWDHURY, Jaminibhusan.—See Priyadarajan RAY.
- SAHASRABUDHEY Ramchandra and Hans KRALL.—The phenylthiocarbamides. A contribution to the study of the triad-N.C.S. Part X. Action of hydrolytic agents, alkaline lead acetate and nitrous acid on thiosemicarbazide ... 225
- SALAH-UD-DIN.—See Rafat Husain SIDDQUI.
- SARUP, Mahendra.—See S. S. BHATNAGAR.
- SEHGAL, R. P.—See K. N. GAIND.
- SEN, Amitabha.—See Jnanendra Nath MUKHERJEE ; B. CHATTERJEE.
- SEN, Dinesh Chandra.—Studies in the camphor series. Part VI. ... 76
- SEN H. K.—Resin plastics ... 47
- SEN-GUPTA, N. C. and P. R. SINHA.—On the moving boundary methods for the determination of cataphoretic speed of colloids. Part I. ... 489
- SETH, S. R.—See V. S. PURI.
- SHAH, N. M.—See D. R. KULKARNI.
- SHAH, R. C.—See T. B. PANSE.
- SHUKLA, J. P.—Studies in enzymes. Amylase from kaseru (*Scripus grossus*. Linn) ... 407
- SIBAIYA, L. and M. S. Venkatasubba RAO.—Spectrum analysis of mineral contents of fruits ... 523
- SIDDQUI, Rafat Husain.—A note on an isomer of dimethylpyridine ... 505
- SIDDQUI, Rafat Husain and SALAH-UD-DIN.—Studies in the substituted succinic acids. Part I ... 635

- SIDDQUI, S. and Z. AHMAD.—A note on the new formula for thalictine 589
 —See also Shiam Kishore VASHISTHA
 SIDDHANTA Susil Kumar.—See Priyadarshan RAY
 SINGH, Arjan.—See Mahan SINGH
 SINGH, Damri.—See Dushyant Narasingasa SOLANKI
 SINGH, Mahan and Arjan SINGH.—Studies on optical activity and chemical constitution. Part V. Rotatory powers of camphor anilic acids, α - and β -naphthylcamphoramic acid at various degrees of neutralisation 89
 SINGH, Surjit.—See R. K. BAHL
 SINHA, P. R.—See N. C. SEN-GUPTA
 SINHA, Ramani Mohan.—See Paresh Chandra DUTTA
 SOLANKI, Dushyant Narasingasa and Bhaskar Govind JOSHI.—Electrodeposition of cadmium on iron 177
 SOLANKI, Dushyant Narasingasa and Damri SINGH.—Studies of some physical factors in the electrodeposition of nickel on iron 423
 SOLANKI, Dushyant Narasingasa and T. V. SUBBARAO.—A note on the electrolytic estimation of lead as peroxide 45
 SRINIVASAN, K.—See Shridhar Sarvottam JOSHI
 SRIVASTAVA P. D.—See N. N. GODBOLE
 SUBBARAO, T. V.—See Dushyant Narasingasa SOLANKI
 SULAIMAN, M.—The influence of light on nitrogen fixation in Dacca soil 46
 SURI, H. D., Gurcharan Singh AHLUWALIA and H. B. DUNNCLIFF.—The detection and determination of pyridine bases in denatured spirit 273
 —Determination of copper in country spirits 326
 TRIPATHI, R. C.—On a relationship between refractive index and surface tension 411
 VAISH, B. L.—See Kesho Dass JAIN
 VARADANAM, Ch. I.—See G. GOPALARAO
 VASHISTHA, Shiam Kishore and Salimuzzaman SIDDQUI.—Chemical examination of *Thalictrum foliolosum* D. C. Isolation and characterisation of a new alkaloid thalictine 641
 WHEELER, T. S.—See T. B. PANSE
 YAJNIK, N. A.—See S. S. BHATNAGAR

Journal of the Indian Chemical Society

Vol. XVIII, 1941.

SUBJECT INDEX

A

	PAGE
Acetone dicarboxylic acid [<i>para-methyl</i> (<i>p</i>)tolylcarbonyl]dianilide (DAS-GUPTA & GHOSH) ...	121
Acetonitrile, a new method of preparation of (GWAN) ...	164
Acridine, 2(3)-(4'-acetylaminobenzene)-sulphonamido-7-methoxy-5-chloro- (DAS-GUPTA) ...	27
Acridine derivatives (DAS-GUPTA) ...	25
with mercury, copper and antimony compounds (DAS-GUPTA) ...	93
Activated sugar charcoal coated with various organic substances, properties of and catalytic decomposition of hydrogen peroxide by (ACHARYA) ...	15
Adsorption of hydroxybenzenes by sugar charcoal (JAIN & JHA) ...	535
Adsorption of polybasic organic and inorganic acids by sugar charcoal (JAIN & JHA) ...	321
Aluminium chromate, normal (RAYCHOUDHURY) ...	573
Aminobenzene sulphonacetamide, N ⁴ -(2-chloro-7-methoxy-, 7-methoxy)-acridyl- (DAS-GUPTA) ...	28
Aminobenzene sulphonamide, N ⁴ -(2-chloro-7-methoxy)-acridyl- (DAS-GUPTA) ...	27
Aminobenzene sulphon-diethylamine, N ⁴ -(2-chloro-7-methoxy-, 7-methoxy)-acridyl- (DAS-GUPTA) ...	28
2-Amino-3:4-tetrahydrobenzothiazole (BASU & DAS-GUPTA) ...	167
Ammonia, photosensitised oxidation of, in aqueous solution with titania (GOPALARAO & MURTY) ...	127
(GOPALARAO & VARADANAM) ...	351
Ammonium nitrate-ammonium sulphate-water system at 25° (BAHL and SINGH) ...	307
Amylase from Kaseru (<i>Scirpus grossus</i> , Linn) (SHUKLA) ...	407
Ascorbic acid, complex formation of, with formaldehyde (KRISHNA-MURTHY) ...	383
Atropine, colorimetric method for determining (DAROGA) ...	579

B

Base exchange of mercuric ions absorbed on wool (NARWANI & GURSAHANI) ...	527
---	-----

- p*-Benzenesulphonamide : (acetylamino-), *o*-anilino-, *o*-toluidino-
(*o*-, *m*-, *p*-) *o*-anisidino-, (*o*-, *m*-, *p*-) *o*-phenitidino (*o*-, *m*-, *p*-), *o*-*o*-
xylydino-, *o*-5-aminoquinolino-, *o*-diethylamino (GAIND, SEHGAL & RAY) 209
- Benzoic acid, (5)-(p-acetylaminobenzene)-sulphonamido-, 2-chloro-
(DAS-GUPTA) ... 26
- Benzoic acid, 2-chloro-4-amino-, 2-chloro-5-amino- (DAS-GUPTA) ... 26
- Benzonitrile, a new method of preparation of (GWAN) ... 164
- 1-Benzylidenecoumaran-2-ones (PANSE, SHAH & WHEELER) ... 453
- Buchanania Latifolia*, the seed fat of (GODBOLE, GUNDE & SRIVASTAYA) ... 558
- Biguanide metal complexes, constitution of (RAY & SIDDHANTA) ... 298
- Biguanide sulphate as a reagent for the estimation of copper. (RAY and
ROY-CHOWDHURY) ... 149
- Cadalene, a new synthesis of (DUTTA) ... 233
- Cadmium, electrodeposition of, on iron (SOLANKI & JOSHI) ... 177
- Camphor series, studies in (SEN) ... 76
- Catalysis of the reaction between ammonium oxalate and mercuric
chloride by ferric ions (BHATNAGAR, KAPUR, BHATNAGAR & PRAKASH) 371
- Cataphoretic speed of colloids, (SEN-GUPTA & SINHA) ... 489
- Chaksine, a new formula for (SIDDIQUI & AHMAD) ... 589
- Chemotherapy of bacterial infections (RAO) ... 316
- Chlorate ion, a new colorimetric method for (ROY) ... 165
- Chlorination of chloroform to carbon tetrachloride in presence of
ferric chloride (BHATNAGAR, YAJNIK, KAPUR & BHATNAGAR) ... 350
- Chlorine, action of, on the hydroxides of iron and chromium in
presence of iodine (BAHL & LAL) ... 359
- p*-*o*-Chloroacetylaminobenzenesulphonyl chloride, condensation with
aniline, diethylaniline, toluidine (*o*-, *m*- and *p*-) and *p*-anisidine
(GAIND, SEHGAL & RAY) ... 211-212
- Chromi-selenates, dehydration of some pure and mixed, and the
formation of corresponding complex chromi-selenic alums (RAY-
CHOUDHURY) ... 277
- Chromium trisbiguanidinium hydroxides, action of mercuric chloride
and silver nitrate upon (RAY & SIDDHANTA) ... 298
- Cinnamic acid, β -methyl- α (β -chlorovinyl)-, 2:4-dimethoxy-, 2:3:4-
trimethoxy (KULKARNI, ALIMCHANDANI & SHAH) ... 116-118
- Cobaltic trisbiguanide complex, resolution of, into its optically active
enantiomerides (RAY & DUTT) ... 289
- Cobaltic trisbiguanidinium hydroxides, action of mercuric chloride and
silver intrate upon (RAY & SIDDHANTA) ... 298

- Colloids, coagulation of, by exposure to high frequency oscillations
(JOSHI & PURUSHOTTAM) ... 138
- Conductometric method of determining the soluble salt content in soils
(HOON, MALHOTRA & JAIN) ... 103
- Copper, a new reagent for the estimation of (DAS-GUPTA) ... 43
determination of, in country spirits (SURI, AHLUWALIA and
DUNNICLIFF) ... 326
- Coumaran-2-one, 1-bromo-1-(ω -bromo-*p*-methoxybenzyl)-, action of
alcohol and of alkali on (PANSE, SHAH & WHEELER) ... 454
- Coumaran 2-one, 1-*p*-anisylidene-, condensation of, with cyclohexanone,
desoxybenzoin, and ethyl acetoacetate (PANSE, SHAH & WHEELER) ... 455
- Coumarin, 3-(β -chlorovinyl)-4-methyl-, 7-hydroxy-, 7:8-dihydroxy-
and 4:6-dimethyl- (KULKARNI, ALIMCHANDANI & SHAH) ... 115-118, 125
- Coumarin, 3(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-4-methyl-, 7-hydroxy-
7:8-dihydroxy-, 5-hydroxy-4:7 dimethyl-, 5:7-dihydroxy-, and their
derivatives (KULKARNI, ALIMCHANDANI & SHAH) ... 115-118
- Cyanin dyes, sensitisation spectra of, derived from α -picoline (DOJA) ... 281

D

- Decalene-3-carboxylic acid, 2-keto-8-methyl-, and ethyl ester
(CHATTERJEE & BOSE) ... 199
- β -Decalone, (8-methyl-), (CHATTERJEE & BOSE) ... 199
- 1:1-Dimethyl- Δ^8 -hepta (and octa) decenol-1 (MITTER & BAGCHI) ... 463, 462
- Diphenylamine-2- carboxylic acid, 4(5)-(p-acetyl aminobenzene)
sulphonamido-4-methoxy- (DAS-GUPTA) ... 26

E

- Electrochemical preparation of sodium chlorate (JOSHI & SRINIVASAN) ... 623
- Electrodeposition of cadmium on iron (SOLANKI & JOSHI) ... 177
of nickel on copper and effect of colloids in (PURI & SRTH) ... 465
of nickel on iron (SOLANKI & SINGH) ... 423
- Equilibrium in systems of iodine and various unsaturated organic
compounds in the dark in different non-polar solvents (GHOSH,
BHATTACHARYYA, DUTT & RAO) ... 171
- Ethyl acrylate, α -cyano- β -(*o*-chlorophenyl-, *p*- and *v*-methoxyphenyl-,
phenyl-)- (SIDDIQUI & SALAH-UD-DIN) ... 636, 638
- Ethyl acetoacetate, α (α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-, the Pechmann
condensation of (KULKARNI, ALIMCHANDANI & SHAH) ... 113, 123
- Ethyl (γ -*p*-tolyl)- β -hydroxyvalerate (DUTTA) ... 236
- Eudalene, a new synthesis of (CHATTERJEE & BOSE) ... 196

F

Ferrous and ferric iron in minerals, microanalytical method for the estimation of (DAS-GUPTA) ... 375

G

Glucose and iodine in alkaline medium, effect of neutral salts on the reaction between (JAIN & VAISH) ... 503

H

Δ^7 -Heptadeconic acid, methyl ester of (MITTER & BAGCHI) ... 462

Δ^8 -Hexadecenoic acid, synthesis of (MITTER & BAGCHI) ... 461

*cyclo*Hexane (6-methyl-)-1-acetic acid (and 1-ol)-2-propionic acid, diethyl ester of (CHATTERJEE & BOSE) ... 199, 198

*cyclo*Hexanone (6-methyl-)-2- β -propionic acid (CHATTERJEE & BOSE) ... 198

*cyclo*Hexanone (6-methyl-)-2-carboxylic acid-2-propionic acid, diethyl ester of (CHATTERJEE & BOSE) ... 197

*cyclo*Hexylidene (6-methyl-)-1-acetic acid-2-propionic acid, derivatives of (CHATTERJEE & BOSE) ... 199

Hydrogen bentonite sols, variation of electrochemical properties of with temperature (MUKHERJEE, CHATTERJEE & SEN) ... 283

Hydrogen bond formation (amides) (SUNDARA RAO) ... 337

Hydrogen clay sols, variations of electrochemical properties of with temperature (CHATTERJEE & SEN) ... 646

Hydrogen sulphide, action of, on permanganates (MOHAMMED & AHLUWALIA) ... 309

I

Induced circular dichroism in vanadic acid sol (RAMA CHAR) ... 605

Iodination (GHOSH, BHATTACHARYYA, DUTT & RAO) ... 171, 245

(BHATTACHARYYA & RAO) ... 253

(BHATTACHARYYA) ... 257, 266

Iodine, estimation of, in periodates (BAHL, SINGH & BALI) ... 587

K

Kinetics of hydrogenation of oils in a continuous process (JOGLEKAR & JATKAR) ... 631

L

Lead, electrolytic estimation of (SOLANKI & SUBBA RAO) ... 45

M

	PAGE
Magnetic susceptibilities of metallic oxides and their molecular structures with special reference to those of cobalt (BHATNAGAR, PRAKASH & QAYYUM)	540
Magnetism and catalysis (BHATNAGAR, VAJNİK, KAPUR & BHATNAGAR) ...	350
(BHATNAGAR, KAPUR, BHATNAGAR & PRAKASH) ...	371
(BHATNAGAR, KAPUR, BHATNAGAR & QAYYUM) ...	391
Mercury, a new reagent for the estimation of (DAS-GUPTA) ...	43
Mercury compounds, co-ordinated with ethylene and propylene-diamines (NEOGI & MONDAL)	146
Methyleneglycol, mono-ethers of (GUPTA, KAUSHAL & DESHPANDE) ...	638
Methyl <i>no</i> -hydrastinine, condensation of, with piperonal, veratric aldehyde, anisaldehyde, propionic aldehyde, acetone, acetaldehyde and cotarnine (GAIND, KAPOOR & RAY)	214-216
Mineral contents of fruits, spectrum analysis of (SIBATYA & RAO) ...	523
Molal volumes (apparent), of electrolyte mixtures in aqueous solution (CHAKRAVARTI & PRASAD)	239
Morphine, the azo compounds from (ROY)	29
Moving boundary method for the determination of cataphoretic speeds of colloids (SEN-GUPTA & SINHA)	489
Muscovite mica (spotted), microchemical investigations on (DAS-GUPTA)	381

N

1:2- α -Naphthapyrone, 4-methyl -3- (α -hydroxy- $\beta\beta\beta$ -trichloroethyl)- (KULKARNI, ALIMCHANDANI & SHAH)	118
Nickel biguanidines (RAY & PURAKAYASTHA)	217
Nickel sulphate, velocity of hydration and dehydration of (GHOSH) ...	472
Nitrogen fixation in Dacca soil, the influence of light on (SULAIMAN) ...	40
Nitroso derivatives, as reagents in inorganic analysis (GUHA-SIRCAR & BHATTACHARJEE)	155 161,

O

Oxalenediamidoxime, metallic derivatives of (CHATTERJEE) ...	19
Oxanilic acid thioamide as an analytical reagent (MAJUMDAR) ...	419
Oxymethylenethiocamphor (SEN)	79
Oxymethylene methylethyl (β -phenyl) ketone, structure of (JOSHI, KAUSHAL & DESHPANDE)	479

- Oxymethylene methyl ethyl (phenyl) ketone, condensation with
cyanoacetamide (JOSHI, KAUSHAL & DESHPANDE) ... 482-483

P

- Paramolybdates, composition and constitution of (RAY & SIDDHANTA) 397
- γ -(*p*-Tolyl)- Δ^8 -pentenoic acid, ethyl ester (DUTTA) ... 236
- Periodates of quadrivalent and trivalent metals (RAYCHOUDHURY) 335, 576
- 9:10-Phenanthrathiophene -2':4':5'- tolazine (DUTTA & SINGH) 477
- 9-Phenanthrathiophene -2':3'- dione- (DUTTA) ... 471
- Phenanthrathiophene -2':3'-dione, azine dyes derived from (DUTTA & SINGHA) ... 477
- 9:10-Phenanthrathiophene-phenazine (DUTTA & SINGHA) ... 478
- Phenanthrene-9-disulphide (DUTTA) ... 470
- Phenanthrene, 9-thiol-, derivatives of (DUTTA)... 469
- Phenols, condensation of α -substituted acetoacetate with (KULKARNI, ALIMCHANDANI & SHAH) ... 113, 123
- Phenylbiguanidines of copper and nickel and their different modifications (RAY & CHAKRAVARTY) ... 609
- Phenylthiocarbamides (SAHSRABUDHEEY & KRALL) ... 225
- Photochemical activity of mixtures of vanadic acid and tartaric acid (RAMA CHAR) ... 507, 563, 605
- Photosensitisation by solids (GOPALARAO & MURTY) ... 127
- (GOPALARAO & VARADANAM) ... 361
- Photosensitised oxidation of ammonia in aqueous solution with colloidal titania (GOPALARAO & VARADANAM) ... 361
- (GOPALARAO & MURTY) ... 127
- Potassium chlorate, magnetic study of the catalytic decomposition of, by cobaltous oxide and ferromagnetic variety of ferric oxide (BHATNAGAR, KAPUR, BHATNAGAR & QAYYUM) ... 391
- Potassium nitrate, decomposition of, in sunlight (SUBBARAO & GOPALARAO) ... 225
- Prussian and Turnbull's blues, adsorptive properties, role of hydrolysis on the composition and magnetic susceptibility of (BHATTACHARYA) ... 71, 76, 85
- Pyridine, 2:4-dihydroxy -3- phenylcarbamido-6-methyl- (DAS-GUPTA & GHOSH) ... 121
- Pyridine bases, detection and determination of, in denatured spirit- (SURI, AHLUWALIA & DUNNICLIFF) ... 273
- Pyridine dimethylethyl, an isomer of (SIDDQUI) ... 505
- Pyridino (2- hydroxy -6-methyl)-3:4 (3':4') -2 hydroxyquinoline disulphonic acid (DAS-GUPTA & GHOSH) ... 121

Q

	PAGE
Quinoline derivatives (DAS-GUPTA & GHOSH) ...	120
Quinoline -8- carboxylic acid as an analytical reagent (MAJUMDAR) ...	419
isoQuinoline derivatives, a new method of synthesis of (GAIND. KAPOOR & RAY) ...	213
Quinoxalino-9:10-phenanthrathiophenazine (DUTTA & SINHA) ...	478

R

Raman spectra of substituted sulphuric acids (GUPTA & MAJUMDAR) ...	457
<i>Rauwolfia Canescens</i> , Linn, the alkaloids of (MOOKERJEE) ...	33, 485
Rauwolscine (MOOKERJEE) ...	36
Rauwolscinic acid and derivatives (MOOKERJEE) ...	38, 487-88
Relation between surface tension and refractive index (TRIPATHI) ...	411
Resin plastics (SEN) ...	47
Resins (synthetic), adsorptive properties of (BHATNAGAR & SARUP) ...	447
Rhythmic precipitation of silver chloride in gelatin tanned with chromium chloride (NARWANI & GURSAHANI) ...	531
Rotatory powers of camphoranilic acids, α - and β - naphthylcamphoramic acid at various degrees of neutralisation (SINGH & SINGH) ...	89

S

Salt content (soluble) of soils, the conductometric determination of (HOON, MALHOTRA & JAIN) ...	103
Sensitisation spectra of certain cyanin dyes (DOJA) ...	281
Separation of silicon and tin in tin-silica mixture, welding brasses and silicon brasses by alkali sulphate (CHATTERJEE) ...	591
Silicic acid sol, variation of the electrochemical properties of, with temperature (MUKHERJEE, CHATTERJEE & SEN) ...	283
Silver chloride, rhythmic precipitation of, in gelatin tanned with chromium chloride (NARWANI & GURSAHANI) ...	531
Sodium chlorate, electrochemical preparation of (JOSHI & SRINIVASAN) ...	621
<i>Solanum Indicum</i> , Linn, the fatty oil from the seeds of (PUNTAMBEKAR & KRISHNA) ...	329
Succinic acid, phenyl-, <i>o</i> -chlorophenyl-, <i>o</i> -methylphenyl-, <i>p</i> -methoxyphenyl-, and their derivatives (SIDDIQUI & SALAH-UD-DIN) ...	635
Sulphanilamides, N^1 -(ac-tetrahydro- β - naphthyl)-, N^1 -(4- β - amineoethylphenyl)-, and derivatives (RAO) ...	320
Sulphanilamides, N^1 - β -phenylethyl-, 4-methoxy-, 3:4-dimethoxy, 4-nitro-, 4-amino-, and their acetyl derivatives (RAO) ...	318-320

2-Sulphanilamido-3:4-tetrahydrobenzothiazole (BASU & DAS-GUPTA)	168
2-Sulphanilamido-4-methylthiazole (BASU & DAS-GUPTA)	... 168

T

Ternary system, Ammonium nitrate-ammonium sulphate-water at 25°	
(BAHL & SINGH)	307
1:2:3:4-Tetrahydrophenanthrene, 1-keto-4:7-dimethyl- (DUTTA)	... 237
Thalictrine and its derivatives (VASHISTHA & SIDDIQUI)	... 644-645
<i>Thalictrum Foliosum</i> , chemical examination of (VASHISTHA & SIDDIQUI)	... 641
Thiocamphor <i>o</i> -carboxylic acid and α -dithiocarboxylic acid and derivatives (SEN)	... 78, 79
5-Thiolacridine, 2-chloro-7-methoxy-, mercury, copper and antimony compounds with (DAS-GUPTA)	... 94-96
Thiosemicarbazide, action of hydrolytic agents, alkaline lead acetate and nitrous acid on (SAHASRABUDHEY & KRALL)	... 225
(<i>p</i> -Tolyl)-propionaldehyde (DUTTA)	... 235
(<i>p</i> -Tolyl)-methylglycide ester (DUTTA)	... 235
Turnbull's and Prussian blues, composition, adsorptive properties and magnetic susceptibilities of (BHATTACHARYA)	... 71, 76, 85

V

Vanadic and tartaric acid mixtures, reduction of, in light and in dark	
(RAMA CHAR)	507
induced optical activity by circularly polarised light in	
(RAMA CHAR)	563
Vitamin-C, retardation of oxidation of, by oxalic acid (KRISHNAMURTHY)	201
catalytic oxidation of, by substances occurring in plant	
and animal tissues on (KRISHNAMURTHY & GIRI)	... 191
the influence of, on the inactivation of enzymes by	
ultraviolet light (GIRI)	... 141
co-existence of oxidising and protective factors in plants	
for (KRISHNAMURTHY & GIRI)	... 7

ERRATA

Page.	Line.		
327	5	After (10 per cent w/w)	Insert " and 3 ml. of dilute nitric acid"
	23	After 4%	Insert " potassium ferrocyanide and 5 ml. of 10%"
328	0	For " citric "	Read " citric acid"
	12	„ " of $p_{H} 9$ "	„ "to $p_{H} 9$ "
	13	„ " 0.1, 0.4" etc.	„ "0.1, 0.2, 0.4" etc.
421	Table I	Delete the 6th place after the decimal point and increase the 5th place by one.	
	Table II, 9th column	For	Read
		-0.00029	-0.000295
		0.00478	-0.000485
422	Table III, 9th column	„	„
		-0.000012	-0.00001
		-0.000027	-0.00003
		+0.000037	+0.00004
		+0.000053	+0.00005
		+0.00006	+0.00001
422	11*	„ "normal acetic acid"	„ "acetic acid"
471	Structural formula III		

